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The Chairman introduced the authors and the following paper was presented in summary by Mr Griffiths.

THE PART PLAYED BY THE PREPARATIONAL STAGE IN DETERMINING LEAD ANTI-KNOCK EFFECTIVENESS *

By D. DOWNS † (Associate Fellow), S. T. GRIFFITHS ‡ (Associate Fellow), and R. W. WHEELER †

SUMMARY

There are at least two processes which go to make up the overall anti-knock action of tetraethyl lead: (1) the preparational, which ensures that the organic molecule decomposes to the active inorganic form at the right time and in the right state for maximum effectiveness; and (2) the inhibiting, which determines the inherent anti-knock capabilities of the active lead in the given set of circumstances. For this investigation into the preparational stage, an electromagnetically-operated sampling valve was used to extract samples of gas from the combustion chamber of the engine at different times in the cycle. Analyses of these samples enabled the decomposition of tetraethyl lead to inorganic lead compounds within the engine cylinder to be followed. At the same time, motored engine experiments were carried out to provide information on the cool and hot flame limits and cool flame intensities of the fuels used for the TEL decomposition tests.

A preliminary experiment, using a Tyndall beam technique, demonstrated that a fog of inorganic lead particles is formed in the engine cylinder sufficiently early to influence the chemical reactions leading to knock.

The lead sampling investigation showed that fuel type has an important influence on the decomposition of TEL from the organic to the inorganic form. Thus, under fixed engine conditions, the higher the knock rating of the fuel, the later the TEL decomposition. The timings of cool flame formation and of TEL decomposition suggest that the cool flame plays some part in decomposing the TEL to the active form. There would not, however, appear to be a very close relationship between TEL decomposition and cool flame intensity, and it is concluded that the influence of the cool flame should not be considered in isolation from the other factors, such as pre-cool flame oxidation and adiabatic compression, which contribute to the overall temperature rise in the end-gas at the time of TEL decomposition.

When the severity of the engine operating conditions is increased, by raising the compression ratio to the knock limit for all fuels, the TEL decomposition is advanced to a sufficiently early timing to ensure the presence of a lead fog during the knocking reactions, even with fuels of poor lead response, such as benzene and methanol. Even the addition of ether to these fuels, which increased their cool flame intensities and their lead responses, had no effect on the timing of TEL decomposition with benzene and only a small effect with methanol. Thus, while it is broadly true that the earlier the decomposition of the tetraethyl lead, the better the lead response of the fuel, the scatter of results is sufficiently great to suggest that this is by no means the only factor involved.

It would appear, therefore, that of the two aspects of TEL anti-knock activity, the preparational and the inhibiting, the latter is probably the more important.

INTRODUCTION

THERE is now abundant evidence that tetraethyl lead does not exert its anti-knock effect as an unchanged organic molecule. It is first necessary for TEL to decompose and oxidize to the active PbO form, although whether this is a vapour [1] or a fine dispersion of solid particles,[2] or perhaps both, is still in some dispute. There are, therefore, at least two processes which go to make up the overall anti-knock action of TEL; (1) the preparational, which ensures that the organic molecule decomposes to PbO at the right time and in the right form for maximum effectiveness; and (2) the inhibiting, which determines the inherent anti-knock capabilities of the PbO in the given set of circumstances. That the preparational stage has at least some importance is illustrated by the very different degrees of anti-knock effectiveness of the various organo-lead compounds,[3] which in part at least must be due to their relative ease of decomposition to the active form.

Fuels differ widely in their response to TEL.[4] Some, like the branch-chain paraffins, have good lead responses; others, like the aromatics and alcohols, have poor or even zero lead responses. In some cases the poor lead response is clearly due to the fact that the reactions involved in the oxidation of the particular fuel are such as not to be susceptible to inhibition by a small proportion of metallic additive. Benzene, for instance, inhibits its own oxidation, which, therefore, proceeds as a large number of short chains rather than as the small number of long chains

* MS received 15 February 1960. ‡ The Associated Ethyl Co. Ltd. † Ricardo & Co. Engineers (1927) Ltd.

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characteristic of paraffin oxidation.[5] If, however, the oxidation of the fuel plays any part in the decomposition of the TEL, then it might be expected that part at least of the difference in lead response between different fuels might reside in the preparational stage.

A characteristic of the chemical reactions leading to knock with most fuels is their two-stage nature,[6] the first stage culminating in the formation of a cool flame. TEL seems to have a smaller effect on the reactions leading to the cool flame than it does on the subsequent reactions leading to the hot flame of true ignition. This suggests that the cool flame plays some part in decomposing the TEL to the active form. This suggestion seemed to be supported by a very rough correlation between lead response and cool flame intensity. The aromatics, alcohols, olefins, and naphthenes, which have poor lead responses, also have low cool flame intensities. The paraffins, on the other hand, produce relatively intense cool flames and, in general, have better lead responses than the members of the other groups.

The principal part of the experimental investigation to be described consists of an attempt to follow the decomposition of TEL to inorganic lead compounds within the engine cylinder, and to study the effect of different fuel types and engine operating conditions on the timing and rate of this decomposition. Information was also obtained, on the same engine under the same operating conditions, where possible, of the knock-limited compression ratios and lead responses of all the fuels under investigation. Motored engine experiments were carried out to provide information on the cool and hot flame limits and cool flame intensities of these fuels for comparison with the TEL decomposition information. Further sampling experiments, studying the development of formaldehyde concentration in the end-gas, were carried out in an attempt to determine the time of formation of the cool flame in the fired engine with more certainty. A Tyndall beam technique was used to demonstrate the existence of a fog of inorganic lead particles within the engine cylinder and to obtain information on its time of first formation.

LEAD SAMPLING EXPERIMENTS

The Apparatus and Test Procedure

A Ricardo E.35 variable compression engine was used for the lead sampling experiments. This engine, which is fully described elsewhere,[7] has a bore of 4½ inches and a stroke of 8 inches and, for the purpose of these experiments, was operated at a speed of 1500 rev/min. The compression ratio can be varied between 3·7 and 8·0 while the engine is in operation.

For most of the tests a somewhat high intake air heat of 3·64 kW (equivalent to an intake air temperature of 132° C) was used. This intake air heat was arrived at during the development of the experimental technique in an attempt to ensure consistent sampling conditions by vaporizing all the fuel. Although such a high intake air heat was subsequently found not to be necessary, it was retained for most of the programme to provide continuity with earlier work. A mixture strength 12 per cent richer than chemically correct was used throughout the test programme. This corresponds approximately with the mixture strength giving maximum power output of the engine. A cylinder coolant temperature of 60° C was standardized.

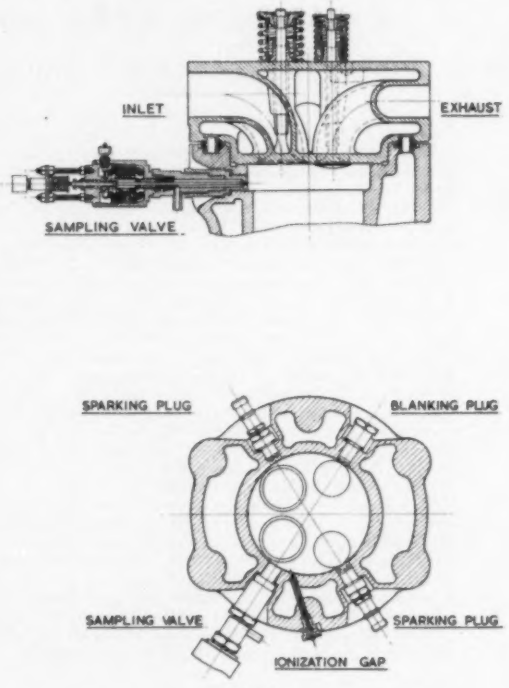


FIG 1

ARRANGEMENT OF THE SAMPLING VALVE IN THE E.35 ENGINE CYLINDER

Fig 1 shows the arrangement of the test equipment on the unit. Two spark plugs were used, and the cyclic variation in the spark timing was reduced to negligible proportions by using, in place of the conventional contact breaker, an electronic triggering mechanism, actuated from a sliding pick-up mounted above the rim of the flywheel and having no mechanical contact with the engine.

The Ricardo sampling valve, which was essentially as described in earlier publications,[6] was fitted in the cylinder wall midway between the two spark plugs and on the side of the combustion chamber where knocking first occurs. The valve is operated by a

solenoid, energized by the discharge of a bank of condensers. This discharge is timed by a contact breaker driven from the crankshaft and which can be adjusted to " make " at any required crank angle position. A second contact breaker, driven from the camshaft and wired in series with the first, ensures that the valve opens only once during each complete cycle. Use of the crankshaft-driven contact breaker as the " master " in this way eliminates possible errors due to backlash in the gears driving the camshaft.

The timing of the valve opening and its duration are indicated by a Sunbury magnetic pick-up assembly operating from an extension of the valve needle. The centre (TDC). This approximately corresponds with the ignition timing optimum for maximum power output.

The size of the orifice and the power put through the solenoid of the sampling valve were increased to give a sampling rate, under most conditions, of 425 cc/min. At this throughput the period of opening of the valve was *ca* 10°. At each crank timing to be investigated, the sample was collected over a period of 260 minutes, *i.e.* a total of *ca* 110 litres of sampled gas was passed through the absorbing train. The basis of the method was to collect the total lead sample and estimate separately the organic and inorganic components.

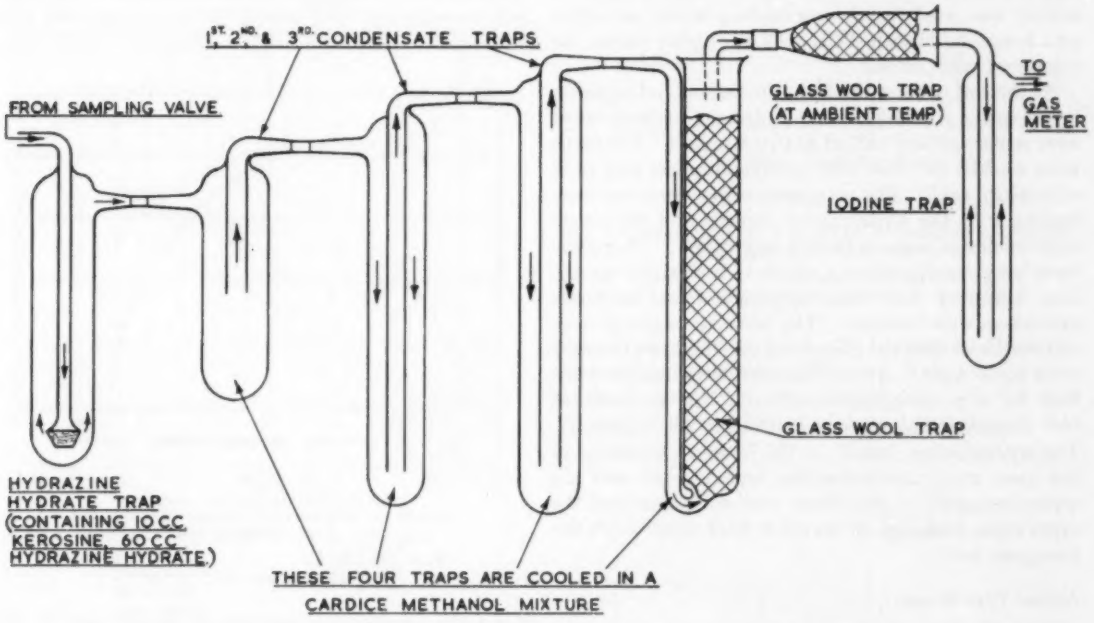

1ST, 2ND & 3RD CONDENSATE TRAPS
FROM SAMPLING VALVE
GLASS WOOL TRAP (AT AMBIENT TEMP)
TO GAS METER
IODINE TRAP
GLASS WOOL TRAP
HYDRAZINE HYDRATE TRAP (CONTAINING 10 CC KEROSINE, 60 CC HYDRAZINE HYDRATE)
THESE FOUR TRAPS ARE COOLED IN A CARDICE METHANOL MIXTURE

FIG 2

LAYOUT OF SAMPLING TRAIN USED ON THE E.35 ENGINE

Ricardo time-base expansion unit enables the valve opening timings to be observed with great accuracy.

An ionization gap is placed in the combustion chamber wall as close as possible to the sampling valve. The ionization current, when placed on the oscillograph, gives the time of flame arrival at the ionization gap. A special test in which a modified sampling valve was itself used as an ionization gap gave the difference in flame arrival between the two points and enabled a correction to be applied to the standard ionization gap readings to give the time of flame arrival at the sampling point. Thus a continued check could be kept on the true time of flame arrival throughout an engine test run. In all these tests the ignition timing was set to give an average flame arrival at the sampling valve of 9° after top dead

Some of the inorganic lead was deposited in the sampling valve itself and was collected on a removable sleeve of nickel foil used as a lining of the sampling valve body. The gas issuing from the sampling valve was passed through the collecting train shown in Fig 2. The first trap contained a 5 per cent solution of hydrazine hydrate in water and was designed to absorb and neutralize all the nitrogen peroxide which would otherwise decompose the organic lead to inorganic lead. This trap also contained a small quantity of kerosine to collect any TEL which might otherwise be entrained in the hydrazine hydrate solution and counted as inorganic lead. The gas issuing from the hydrazine hydrate trap then passed through a series of three condensate traps cooled in a cardice/methanol mixture. When the methanol was

used as a fuel, a small quantity of kerosine was added to each of these traps to ensure that there was an organic component present to absorb TEL. Two glass wool traps and an iodine trap completed the train. The first glass wool trap was cooled in the cardice/methanol mixture. The second, which was designed to collect particulate lead, was uncooled. The iodine trap was intended as a witness that no lead had escaped the earlier traps, as, of course, it was not possible to assign any lead collected in this trap to either the organic or the inorganic component. The quantity of lead recovered in the iodine trap was never greater than 0·3 mg lead and, in most cases, lead was not detected in this trap. Nylon rather than rubber was used for the connecting tubes, as nylon was found to absorb TEL to a negligible extent as compared with rubber.

At the end of the test the hydrocarbon and aqueous layers in the condensate and hydrazine hydrate traps were separated and bulked as two samples. The traps were washed out first with petroleum ether and then with nitric acid. The petroleum ether washings were bulked with the hydrocarbon sample and the nitric acid washings were collected separately. The glass wool was transferred as a whole to a Soxhlet extraction assembly and was subjected to a thorough extraction with benzene. The benzene washings were collected and then the glass wool was further extracted with aqua regia. All the samples were analysed for lead by a polarographic method. The methods of test employed are given in outline in the Appendix. The hydrocarbon sample + the benzene washings of the glass wool constituted the organic lead, and the aqueous sample + the nitric acid washings and the aqua regia washings of the glass wool constituted the inorganic lead.

Initial Test Results

Table I shows a typical set of results for a lead sampling experiment, that for 100/130 Aviation

TABLE I

Ricardo E.35 Engine

Lead Sampling Tests with 100/130 *AG as Fuel*

Test No	316	317	318	319	320	356	369
Sample angle, deg before TDC	50° E	37½° E	25° E	15° E	5° E	15° E	30° E
Sample flow rate, cc/min	435	416	406	415	417	430	397
Period of run, min	255	260	265	260	260	260	275
Total gas collected, litres	111	108·3	107·6	107·9	108·3	111·9	109·2
Deposit weight, mg	7·4	5·6	10·0	2·4	20·0	9·5	9·6
Lead recovery, mg:							
Hydrocarbon layer	12·6	10·4	7·3	5·0	0·8	8·7	14·4
Glass wool trap (organic)	0·7	0·4	0·4	0·2	Nil	0·3	1·1
Iodine trap	Nil	Nil	Nil	0·1	Nil	Nil	Nil
Aqueous layer	0·9	0·7	2·5	2·0	2·3	2·9	1·3
Nitric acid washings	0·3	0·2	0·4	1·2	0·7	0·3	1·2
Glass wool trap (inorganic)	0·5	0·2	Nil	Nil	Nil	1·0	0·3
Nickel foil	0·7	1·2	0·2	1·0	4·7	2·6	0·5
Total	15·7	13·1	10·8	9·5	8·5	15·8	18·8
Percentage organic lead	84·7	82·4	71·3	55·8	9·4	57·0	82·4
Percentage inorganic lead	15·3	17·6	28·7	44·2	90·6	43·0	17·6

Gasoline (AG) at a compression ratio of 5·0. The results have been summarized in Fig 3 in the form of a curve of organic lead concentration against crank timing. It can be seen that the percentage undecomposed TEL (organic lead) is 85 at 50° E, starting to decrease rapidly at 30° E and falling to 10 per cent at 5° E. At a compression ratio of 5·0 something like 20 per cent of the total charge in the cylinder at the beginning of the compression stroke is residual gas left over from the previous cycle. Any lead carried over with these residuals will be inorganic, so it might be said that 85 per cent undecomposed TEL at 50° E represents virtually no decomposition of the TEL induced with the fresh charge for that cycle. As both systems of terminology are used in the later sections of this paper, it might be mentioned at this stage that

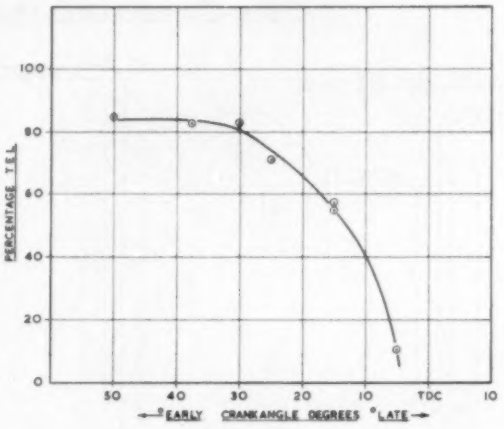


FIG 3

CURVE OF PERCENTAGE UNDECOMPOSED TEL (ORGANIC LEAD) AGAINST CRANK ANGLE

Fuel 100/130 AG CR 5·0

Heat to intake air 3·64 kW

for a compression ratio of 5·0, 80, 60, 40, and 20 per cent organic lead are assumed to be equivalent to 0, 25, 50, and 75 per cent TEL decomposition respectively.

At early crank timings the lead recovery appeared to be satisfactory and to correspond approximately with the nominal TEL content of the fuel. At late timings, however, it was very much less. This is most probably due to the decomposition of lead in the engine cylinder.

Tests at a Compression Ratio of 5·0

Following the initial experiments with 100/130 AG, a wide selection of fuels, both pure hydrocarbons and commercial fuels, were tested at a TEL concentration of 5·5 cc TEL (Aviation Octel)/IG and, initially, at a CR of 5·0.

1. *Pure Fuels.* Taking the pure hydrocarbon fuels first (Fig 4), it can be seen that, as compared with 100/130 AG, the TEL decomposition curve with *iso-*

octane has been shifted earlier by some 10°. With the 67/33 blend of *iso*-octane and heptane and with di*iso*-butylene, on the other hand, TEL decomposition is rather later than with *iso*-octane, with benzene it is even later, and with methanol later still. The result with *cyclo*hexane is rather curious. TEL decomposition starts early with this fuel, but the subsequent rate of decomposition is markedly less than for the other fuels.

2. *Commercial Fuels.* The results for the commercial fuels and blending components are shown in Fig 5. Decomposition of TEL appears to start at much the same time in the cycle for all the fuels, but over the mid-decomposition range there are considerable differences. At 20° before TDC, for instance, the proportion of organic lead is 66 per cent for 100/130 AG, 50 per cent for alkylates and for 100 octane base motor spirit, and 40 per cent for the 170° EP catalytic cracked fuel, a typical component of a modern premium motor fuel. The 100 octane base motor spirit was tested at two lead concentrations, 2 cc/IG and 5·5 cc/IG, and the results in the two cases were very similar.

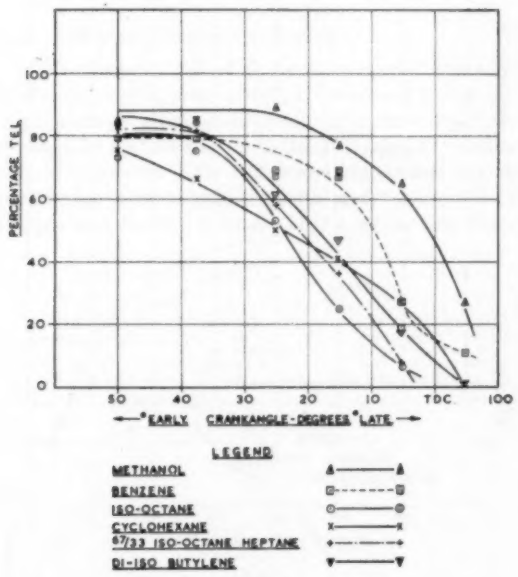


FIG 4

TEL DECOMPOSITION IN A NUMBER OF PURE FUELS
CR 5·0 Intake air heat 3·64 kW
All fuels with 5·5 cc TEL (Aviation Octel)/IG

3. *Lead Scavengers.* To determine the effect of lead scavengers on TEL decomposition, an Aviation Base fuel similar to the base of 100/130 AG was blended and leaded to 5·5 cc TEL/IG with (1) Aviation Octel and (2) pure TEL. Fig 6 shows that TEL decomposition was slightly later with Aviation Octel than with pure TEL. A puzzling feature of the results is that with both mixes TEL decomposition occurred earlier in the cycle than with 100/130 AG. To help throw more

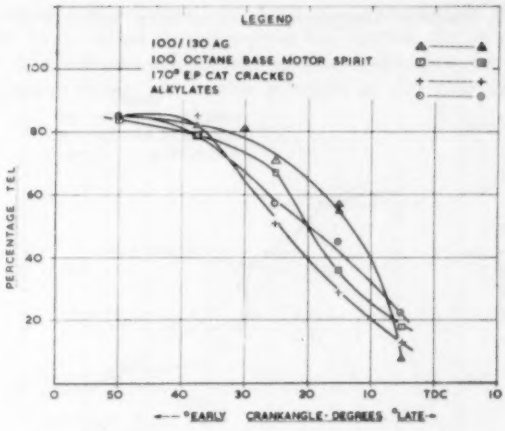


FIG 5

TEL DECOMPOSITION IN A NUMBER OF COMMERCIAL FUELS AND BLENDING COMPONENTS
CR 5·0 Intake air heat 3·64 kW
All fuels with 5·5 cc TEL (Aviation Octel)/IG

light on this and to check the interesting difference observed between pure TEL and Aviation Octel, a series of check tests was carried out. As the first batch of Aviation Base had been exhausted, it was necessary to use a second batch, which was, however, selected to be as nearly as possible the same. The same sort of result was again obtained (Fig 7). With the Aviation Octel, the TEL decomposition occurred

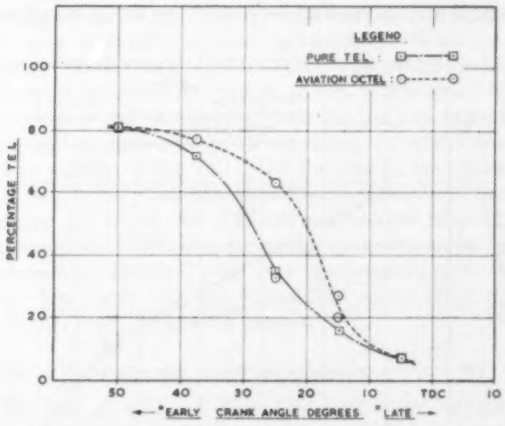


FIG 6

THE EFFECT OF FLUID COMPOSITION ON TEL DECOMPOSITION IN AN AVIATION BASE FUEL WITH 5·5 CC TEL/IG (FIRST TEST SERIES)
CR 5·0 Intake air heat 3·64 kW

earlier in the cycle than with 100/130 AG, and pure TEL decomposed earlier than Aviation Octel. There was little difference between Aviation and Motor Octel.

4. *Sulphur Components.* Di-tertiary butyl tetra-

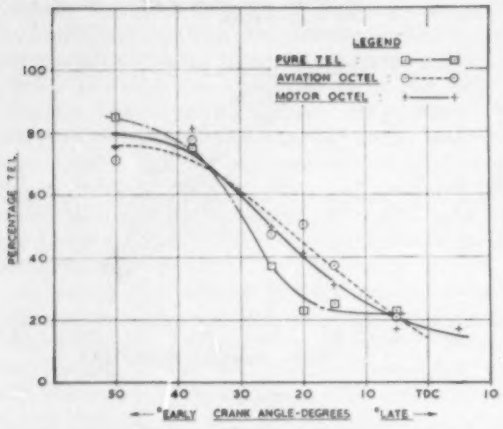


FIG 7

THE EFFECT OF FLUID COMPOSITION ON TEL DECOMPOSITION IN AN AVIATION BASE FUEL WITH 5·5 CC TEL/IG (SECOND TEST SERIES)

CR 5·0 Intake air heat 3·64 kW

sulphide is a well known anti-knock antagonist, and later in this paper some information is given on its effect on the knock-limited compression ratio of *cyclo*hexane and on its lead response. So far as its effect

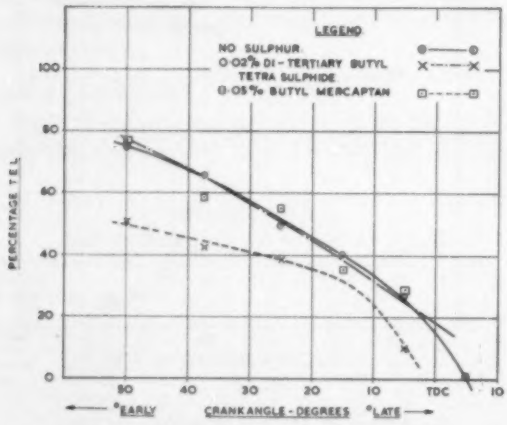


FIG 8

THE EFFECT OF SULPHUR ADDITION ON TEL DECOMPOSITION IN *CYCLO*HEXANE FUEL WITH 5·5 CC TEL (AVIATION OCTEL)/IG

CR 5·0 Intake air heat 3·64 kW

on TEL decomposition is concerned, Fig 8 shows that even as early as 50° before TDC the percentage organic lead was only 50 per cent as compared with a figure of nearly 80 per cent for the leaded *cyclo*hexane without added sulphur. Another sulphur-containing anti-knock antagonist which was tested at the same time, *n*-butyl mercaptan, was found to be virtually without effect on the TEL decomposition in *cyclo*hexane. It would appear, therefore, that the two sulphur compounds must exert their lead antagonistic effects by somewhat different mechanisms.

5. *Other Additions.* It has already been shown that with benzene and methanol, TEL decomposition occurs later in the cycle than with other fuels.

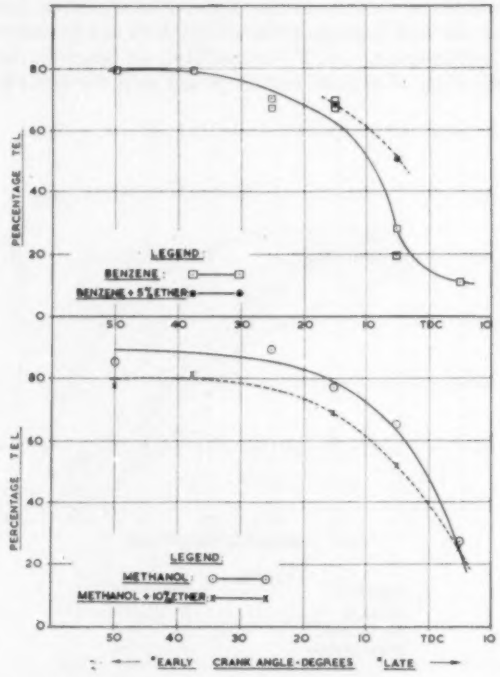


FIG 9

THE EFFECT OF DIETHYL ETHER ADDITION ON TEL DECOMPOSITION WITH METHANOL AND BENZENE AS FUELS

CR 5·0 Intake air heat 3·64 kW
Benzene with 5·5 cc TEL (Aviation Octel)/IG
Methanol with 2·4 cc TEL (Aviation Octel)/IG

Neither of these fuels gives a cool flame, and to obtain further information on the effect of the cool flame on TEL decomposition and on lead response, some tests were carried out with the addition of diethyl ether, which gives an intense cool flame, to those fuels. Motored engine experiments, to be described later, showed in fact that the addition of ether to these fuels did little to promote the cool flame. TEL decomposition curves were, however, obtained with the addition of 10 per cent ether to methanol and 5 per cent ether to benzene (Fig 9). It can be seen that the addition of diethyl ether to methanol causes TEL decomposition to commence somewhat earlier in the

cycle, but that once under way it proceeds more slowly, total decomposition occurring at approximately the same crank angle in the two cases. By a crank timing of 9° after TDC, the arrival of the flame from the spark plug is influencing the TEL decomposition, so that it is not surprising that the latter parts of the two curves should be so similar. The effect of the diethyl ether addition is probably best shown by a comparison of the early parts of the curves.

In the case of benzene, a lower concentration of ether was used, because the motored engine experiments had suggested that ether had a greater effect on cool flame formation in the former case. From the evidence of the few points obtained it would appear that ether, if anything, retards TEL decomposition in benzene, a result very different from that obtained with methanol as fuel.

Tests at Higher Compression Ratios

All the tests described so far were carried out at a fixed compression ratio of 5·0, a value well below the knock limit of most of the fuels under investigation. It could be argued that it is the TEL decomposition at a compression ratio corresponding to the knock limit rather than at a lower compression ratio which is important, as it is, after all, at the former condition

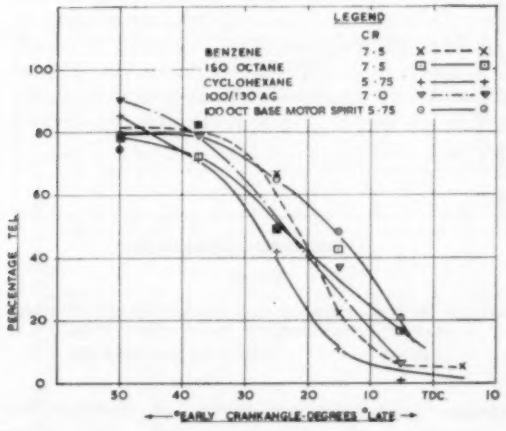


Fig 10

TEL DECOMPOSITION IN A NUMBER OF PURE FUELS AND COMMERCIAL BLENDS AT COMPRESSION RATIOS NEAR TO THEIR KNOCK LIMITS

Intake air heat 3·64 kW
All fuels with 5·5 cc TEL (Aviation Octel)/IG

at which lead has to exert its anti-knock effect. Some of the fuels investigated at a fixed compression ratio of 5·0 were, therefore, the subject of an additional study at a compression ratio just below the knock limit for each individual fuel (Fig 10). The knock limit of benzene is well above 8·0 CR under sampling conditions, so the test was carried out at a CR of 7·5, which is the highest value at which the E.35 engine can be run continuously. Comparing the results at a CR of 7·5 with those obtained at a CR of 5·0, it can be seen that the use of a high compression ratio has very considerably advanced the time of decomposition of the TEL. Once decomposition has started, the rate at which it proceeds is very similar at the two compression ratios. A similar advance in the time of

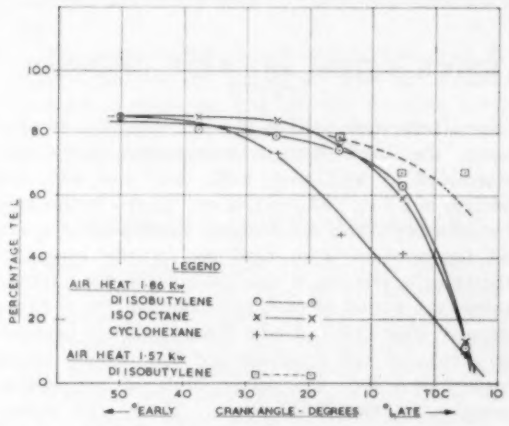


Fig 11

TEL DECOMPOSITION IN A NUMBER OF PURE FUELS AT LOWER INTAKE AIR HEATS

CR 5·0
All fuels with 5·5 cc TEL (Aviation Octel)/IG

decomposition of the TEL was obtained with 100/130 AG, and markedly so with *cyclo*hexane. With *iso*-octane, on the other hand, there was virtually no difference between the curves at CR of 5·0 and 7·5, and raising the compression ratio on the 100 octane base motor spirit seemed, if anything, to retard the decomposition of the TEL. In the case of *iso*-octane this may merely indicate that there are limits to the amount by which the TEL decomposition may be advanced, the TEL decomposition occurring early in the cycle on this fuel even at a compression ratio of 5·0. The result with 100 octane base motor spirit is, however, more difficult to explain.

Tests at Lower Intake Air Temperatures

Because it was felt that the high value of the standard intake air heat may have resulted in some misleading results being obtained, some TEL decomposition curves were obtained on three of the pure fuels with only half the standard air heat. On all three, di-*iso*butylene, *cyclo*hexane, and *iso*-octane, the effect of reducing the intake air heat was to retard significantly the start of TEL decomposition, although, once commenced, it proceeded rapidly so that total decomposition occurred at the same crank timing as with the standard intake air heat (Fig 11).

A further test was carried out with di-*iso*butylene at an even lower intake air heat, and this showed that the lower the intake air heat, the later the TEL decomposition, but the greater the lead response.

Air heat, kw	Air temp (approx), °C	20% Organic lead (*i.e. ca* 25% TEL decomposed)	Lead response, Δ CR
3·64	132	23° before TDC	0·50
1·86	78	4° before TDC	0·80
1·57	70	3° after TDC	0·92

KNOCK RATING AND LEAD RESPONSE TESTS

For all the fuels used in the lead sampling experiments, the knock-limited compression ratio was determined by audibility, both clear and with the addition of 5·5 cc TEL/IG (2·4 cc TEL/IG in the case of methanol). The same engine conditions of speed and temperature were used as for the sampling experiments, and, as in the latter tests, the ignition timing was varied at each condition to give a flame arrival 9° after TDC. Under these conditions benzene and methanol had knock-limited compression ratios greater than 8·0, the upper limit of permissible operation on the E.35 engine. These high rating fuels were, therefore, tested on the E.6 engine [8] (3 inches bore × $4\frac{3}{8}$ inches stroke), where the compression ratio range available was much greater. The conditions of operation on the E.6 engine were arranged to be as closely similar as possible to those on the E.35, and most of the lower rating fuels were tested on both engines to establish a reasonable correlation curve. This curve was then extrapolated, and E.35 ratings corresponding to the particular E.6 figures were read off the curve for the high rating fuels. These extrapolated figures are shown in brackets in Table II.

TABLE II

Knock Rating Tests on the Fuels Used for the TEL Decomposition Experiments

Fuel	E.6 Engine			E.35 Engine		
	Knock limited CR		Lead response	Knock limited CR		Lead response
	Clear	Leaded		Clear	Leaded	
Intake air heat 3·64 kw (E.35 engine)						
Benzene	11·19	11·03	−0·16	(9·02)	(8·90)	−0·12
Benzene + 5% ether	10·50	10·73	+0·23	(8·47)	(8·66)	+0·19
Methanol	10·41	9·77	−0·64	(8·40)	(7·85)	−0·55
Methanol + 5% ether	9·86	9·72	−0·14	(7·93)	(7·82)	−0·11
iso-Octane	7·98	10·5	2·52	6·45	(8·18)	1·73
Di-*iso*butylene	6·83	7·42	0·59	5·12	5·58	0·46
Aviation base	6·69	9·05	2·36	5·3	7·46	2·16
100/130 AG	—	8·74	—	—	7·4	—
100 octane motor base	6·35	7·38	1·03	5·15	6·03	0·88
*cyclo*Hexane	5·90	7·85	1·95	4·77	6·15	1·38
*cyclo*Hexane and 0·02% DTBT	—	—	—	4·73	5·6	0·87
170° EP cat cracked	5·85	7·18	1·33	4·62	5·4	0·78
67/33 *iso*-Octane/heptane	5·09	6·85	1·76	4·29	5·6	1·31
Intake air heat 1·86 kw (E.35 engine)						
iso-Octane	—	—	—	7·42	>8·0	>0·58
Di-*iso*butylene	—	—	—	6·4	7·21	0·81
*cyclo*Hexane	—	—	—	5·62	7·92	2·3
Intake air heat 1·57 kw (E.35 engine)						
Di-*iso*butylene	—	—	—	7·08	8·0	0·92

For the purpose of these experiments the lead response is defined as the difference between the knock-limited compression ratios of the leaded and clear fuels. Of the fuels tested, *iso*-octane had the greatest lead response and di-*iso*butylene the least. The lead responses of the two fuels for which comparative figures exist, di-*iso*butylene and *cyclo*hexane, were improved by lowering the intake air heat. The figures at the two intake air heats also show the extreme temperature-sensitivity of di-*iso*butylene compared with the other fuels tested. The addition of di-tertiary butyl tetrasulphide to *cyclo*hexane reduced the knock limited compression ratios both clear and leaded, but the effect was much greater on the leaded blend, thus lowering the lead response. Benzene and methanol had negative lead responses. The addition of diethyl ether to benzene transformed the slight negative response to a slight positive one, and in the case of methanol somewhat reduced the amount of the negative response.

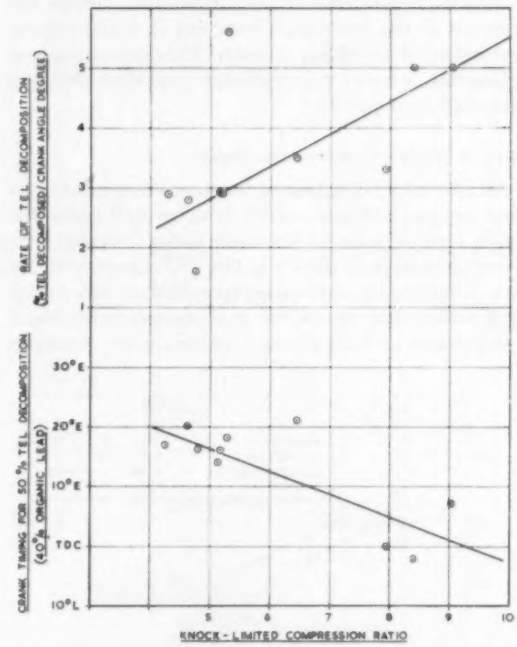


FIG 12

EFFECT OF FUEL TYPE ON TEL DECOMPOSITION (PLOTTED AGAINST KNOCK-LIMITED CR OF CLEAR FUEL)
CR 5·0 Intake air heat 3·64 kW

It can be seen from Fig 12 that there is a very broad relation between TEL decomposition at a compression ratio of 5·0 and the knock-limited compression ratio of the clear fuel. The higher the knock rating of the

fuel, the later in the cycle the TEL decomposes and the greater the rate of TEL decomposition once it starts. The second fact follows from the first, as TEL decomposition is in any case completed by the

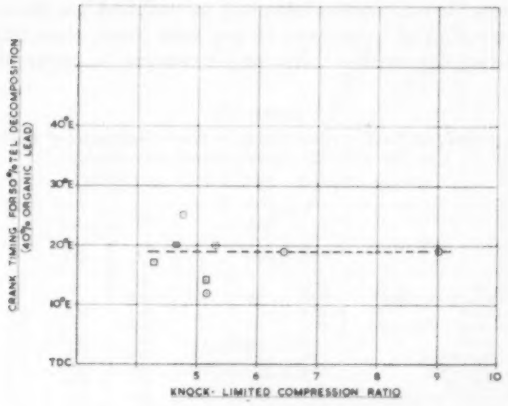


FIG 13

EFFECT OF FUEL TYPE ON TEL DECOMPOSITION (PLOTTED AGAINST KNOCK-LIMTED CR OF CLEAR FUEL)

CR near to knock limit on each fuel (⊡ points at CR 5·0)
Intake air heat 3·64 kW

arrival of the flame, so if the start of TEL decomposition is retarded it must be completed at a greater rate. If, instead of the figures for a compression ratio of 5·0, one considers the TEL decomposition at a compression ratio near to the knock limit in each case (which for some fuels is 5·0), it can be seen that,

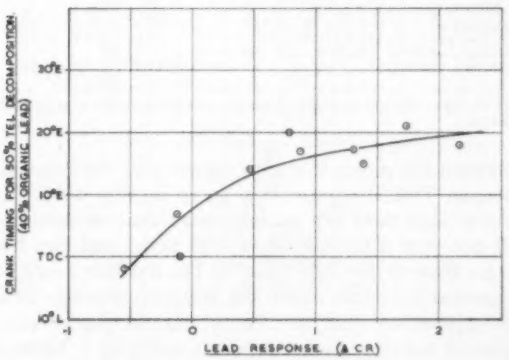


FIG 14

EFFECT OF FUEL TYPE ON TEL DECOMPOSITION (PLOTTED AGAINST LEAD RESPONSE OF FUEL)

CR 5·0 Intake air heat 3·64 kW

although the scatter of points is greater, there is no marked trend for the timing of the 50 per cent decomposition point to vary consistently with the knock rating of the fuel (Fig 13). It remains close to a mean of 19° before TDC in nearly all cases.

The same conclusions may broadly be drawn if the knock-limited compression ratio of the leaded rather than of the clear fuel is considered, but the scatter of points is somewhat greater.

Fig 14 suggests that the earlier the decomposition of the TEL, the better the lead response of the fuel. This relation is most marked when the figures for a compression ratio of 5·0 are considered, but it also seems to hold for the TEL decomposition at the compression ratios near to the knock limit for each fuel.

The same broad general conclusions hold if the figures for the low intake air heat are considered, instead of those for 3·64 kw, but the data available are insufficient to decide whether or not the correlation is improved at the lower temperature.

MOTORED ENGINE EXPERIMENTS

The possible influence of the cool flame on the decomposition of the TEL to an active form was investigated by comparing the measurements of compression ratio for cool and hot flame formation and cool flame intensity, measured in the motored E.6 engine, with measurements of the cyclic time of TEL decomposition made in the E.35 engine. The apparatus and techniques used for the motored engine investigation have been fully described in a previous publication.[9] The Ricardo E.6 engine was motored by means of a variable speed AC swinging-field dynamometer. Electric immersion heaters were used to maintain the crankcase oil and jacket water at the operating temperatures. The fuel was introduced into the engine through a carburettor in the normal way, and the cool flame was detected and measured by means of a photomultiplier coupled to a quartz window inserted through a spark plug hole in the engine cylinder head.

For most of the tests Shell FR hydraulic fluid was used as an engine lubricant, because it permitted higher compression ratios to be used before combustion of the lubricant had an influence on the cool and hot flames of the fuel/air mixtures under investigation.

Test conditions closely simulating those used for the TEL decomposition investigation in the E.35 engine were chosen. Cool and hot flame limit curves and cool flame intensities at the hot flame limit were obtained over the mixture range with the fuels both clear and with the addition of 5·5 cc TEL (Aviation Octel)/IG. In addition, Aviation Base was tested with various mixes and with scavenger only to determine what effect the halides had on these engine combustion reactions.

The limit curves for clear and leaded *iso*-octane are shown in Fig 15. These curves are very similar to those which have been obtained in the past,[9] despite the fact that the operating conditions are somewhat

different. With benzene (Fig 16), the addition of TEL lowered the hot flame limit. No cool flame was observed with either the clear or the leaded fuel. The addition of diethyl ether gave a low intensity cool flame over a wide range of compression ratio and mixture strength, and this was reduced both in extent and intensity by the addition of TEL.

With methanol (Fig 17), no cool flame was detected. A dip in the hot flame limit curve at weak mixtures may have been due to the combustion of lubricant. The addition of TEL had little effect on the minimum

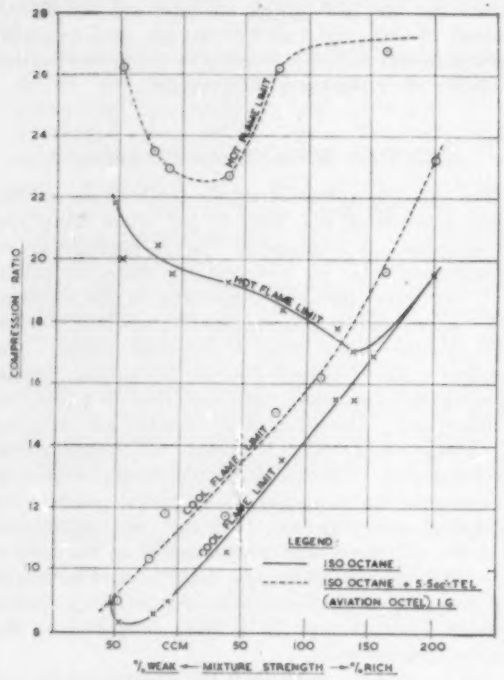


FIG 15

HOT AND COOL FLAME CURVES FOR CLEAR AND LEADED *ISO*-OCTANE

of the hot flame limit curve, but it gave a low intensity cool flame over the whole mixture range. The addition of 10 per cent diethyl ether to clear methanol gave a low intensity cool flame at weak mixtures, at compression ratios near the hot flame limit. The further addition of TEL increased the intensity of the cool flame and the mixture range over which it appeared.

The hot flame limit curves for (1) pure TEL, (2) Aviation Octel, and (3) Motor Octel in Aviation Base are generally similar, but differ in detail. It is difficult to say how significant these differences are because there is considerable scatter of points. The cool flame limit curves are all very similar, but there are differences in intensity at the hot flame limit, the significance of which it is again rather difficult to establish. The ethylene dibromide and ethylene dichloride additions alone seem to have little effect on either the limits or the intensities.

In Tables III and IV is summarized for all these fuels the information obtained on cool and hot flame formation at a mixture 12 per cent richer than the chemically correct. No simple relation is apparent

TABLE III

Cool and Hot Flame Limits and Cool Flame Intensities of Fuels Used for the TEL Decomposition Experiments

Mixture Strength: 12% *Richer than CCM*

Fuel	Clear			Leaded		
	HFL	CFL	I	HFL	CFL	I
Benzene	21·0	—	0	19·0	—	0
Benzene + 5% ether	20·0	9·5	0·5	20·5	—	—
Methanol	21·5	—	—	25·5	24·0	0·5
Methanol + 10% ether	29·0	—	—	26·0	24·4	0·5
iso-Octane	19·5	9·8	4·4	22·6	11·8	2·0
Di-*isobutylene*	21·6	18·0	1·3	23·6	18·0	1·3
Aviation base	13·9	10·0	19·0	19·5	10·9	4·5
100/130 AG	—	—	—	17·7	11·5	1·5
100 octane motor base	18·1	13·7	0·4	18·9	17·1	0·8
*cyclo*Hexane	12·5	10·6	5·0	*ca* 21·0	*ca* 18·0	0
170° EP cat cracked	13·8	10·6	2·0	17·6	12·4	15·0
67/33 *iso*-Octane heptane	9·2	8·0	56	13·9	8·6	47
Alkylates	18·5	10·1	26·0	22·5	10·5	4·5

Note: HFL = Hot flame limit
CFL = Cool flame limit
I = Intensity of cool flame

TABLE IV

Cool and Hot Flame Limits and Cool Flame Intensities of Aviation Base with Various Additions of Lead Mix and Scavenger

Fuel	HFL	CFL	I
Aviation base	13·9	10·0	19·0
Aviation base + 5·5 cc TEL/IG (Aviation Octel)	19·5	10·9	4·5
Aviation base + 5·5 cc TEL/IG (Motor Octel)	18·9	10·8	2·7
Aviation base + 5·5 cc TEL/IG (pure TEL)	18·7	10·8	4·3
Aviation base + IT Ethylene dibromide *	13·8	10·8	20·7
Aviation base + IT Ethylene dichloride *	13·6	9·8	14·0
Aviation base + IT Ethylene dichloride + ½ T. ethylene dibromide *	14·0	9·6	15·2

* Unleaded, but the amount of scavenger added is sufficient to treat 5·5 cc TEL/IG.

between the motored engine figures and the information on TEL decomposition given in Figs 4–11. It is true that there is a general correlation between the 50 per cent TEL decomposition point and the hot flame limit of the clear fuel (Fig 18), but this would be expected to follow from the relation between TEL decomposition and the knock limited compression ratio of the clear fuel, illustrated in Fig 12. There is no very obvious relation between cool flame limit or intensity and the crank timing at which TEL starts to decompose or the rate at which that decomposition subsequently proceeds. This is apart, of course, from the very obvious fact that benzene and methanol, which have low or zero cool flame intensities, have late TEL decomposition and, in the case of methanol at any rate, the addition of ether both increased the cool flame intensity and advanced the timing of the TEL decomposition.

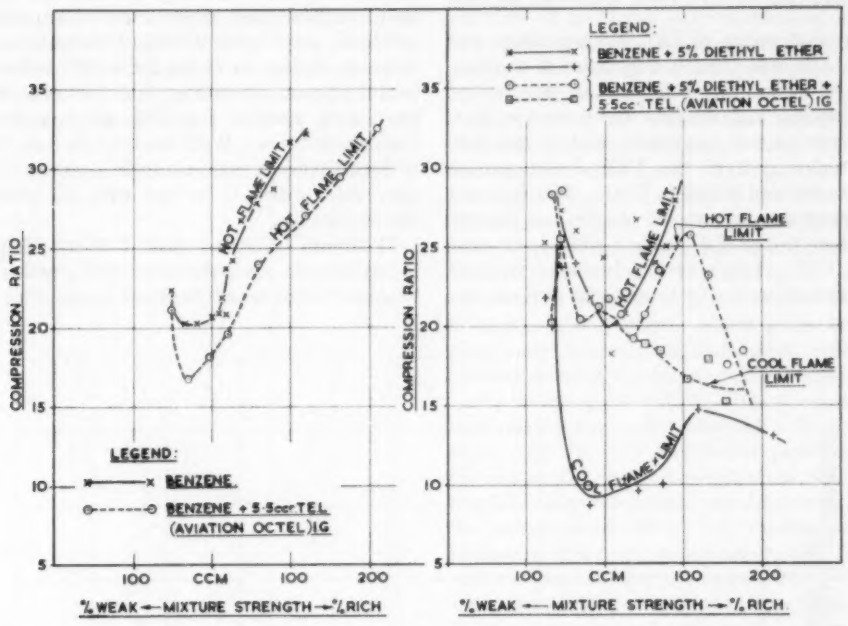


FIG 16

EFFECT OF DIETHYL ETHER ADDITIONS ON THE COOL AND HOT FLAME LIMITS OF CLEAR AND LEADED BENZENE

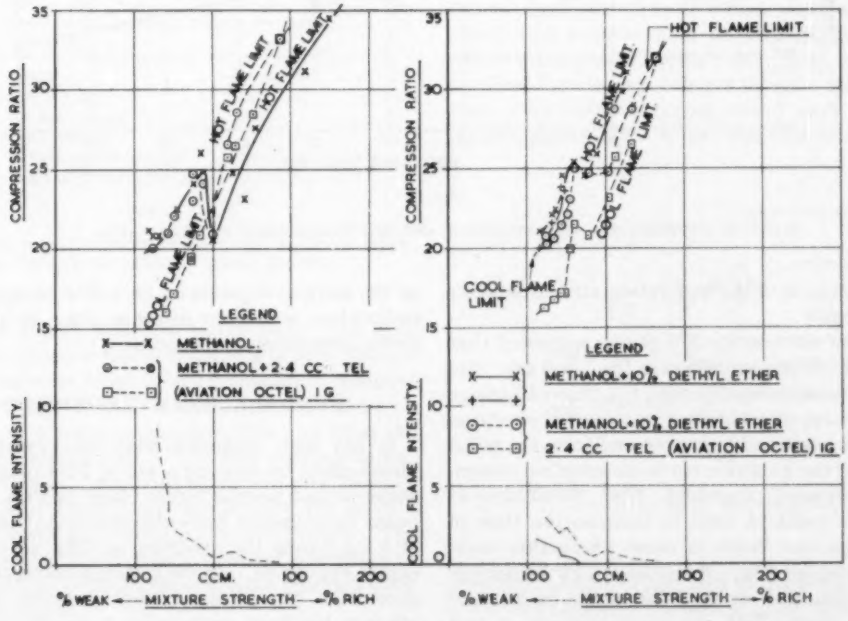


FIG 17

EFFECT OF DIETHYL ETHER ADDITIONS ON THE COOL AND HOT FLAME LIMITS AND COOL FLAME INTENSITIES OF CLEAR AND LEADED METHANOL

FORMALDEHYDE SAMPLING EXPERIMENTS

The timing relationship of TEL decomposition and the passage of the cool flame is important in deciding whether the latter has any influence on the former. The lead sampling experiments have shown that, under the particular test conditions used on the E.35 engine, the major part of the TEL decomposition occurs between 30° and 5° before TDC. This is rather earlier than previous estimates of the time of passage of the cool flame in the E.6 engine,[6] which was some 2° to 3° after TDC. It is probable, however, that the cool flame passes at an earlier time in the cycle on the E.35 engine because of the high intake air temperature used on this unit.

These earlier tests on the E.6 engine suggested that the formaldehyde concentration in the " end gas " did not start to increase rapidly until the time of passage of the cool flame, as estimated by direct observation from motored engine experiments and from the point of inflexion of the peroxide curve in sampling experiments. It seemed, therefore, that formaldehyde concentration could be used to indicate the time of passage of the cool flame in cases where this could not be observed directly. Accordingly, formaldehyde curves were obtained on the E.35 engine for some of the fuels for which TEL decomposition curves had already been obtained. The formaldehyde analyses were carried out using the bisulphite method of Lea.[6] It is difficult to draw any hard and fast conclusions from these results, but Fig 19 would appear to suggest that for those fuels which gave an appreciable formaldehyde development, the concentration starts to increase rapidly at about 20° to 25° before TDC. It would appear, therefore, that the cool flame could play some part in the TEL decomposition process with those fuels. With benzene as fuel, the increase of formaldehyde concentration occurs much later in the cycle, which is in line with its effect on TEL decomposition.

It should be noted that it is the shape of these formaldehyde concentration curves, rather than their absolute value, which ought to be considered because,

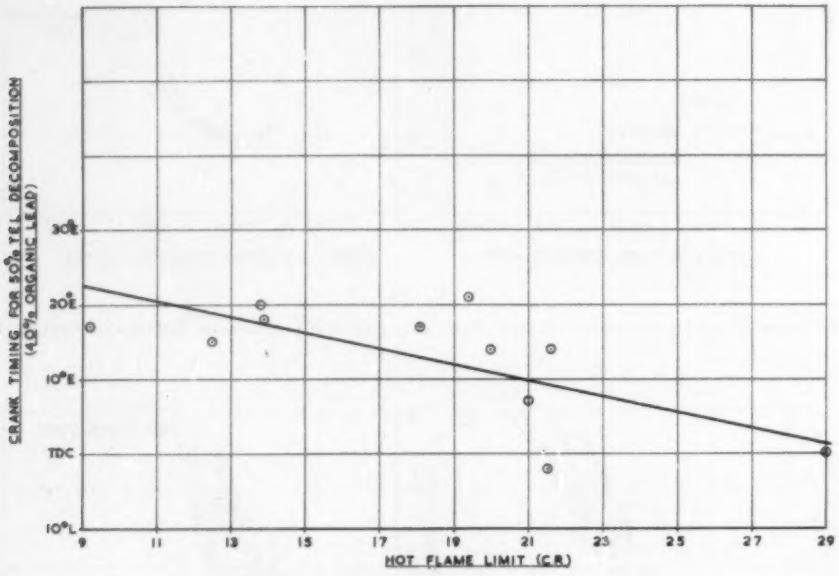


FIG 18

RELATION BETWEEN TEL DECOMPOSITION AND HOT FLAME LIMIT OF CLEAR FUEL

as the method depends on an iodine titration, the di-*iso*butylene curve, for instance, may be high due to olefin absorption of the iodine.

TYNDALL BEAM EXPERIMENTS

It has been suggested that TEL exerts its anti-knock effect by forming a fog of PbO particles which cause surface destruction of chain carriers.[2] Tyndall beam experiments have demonstrated the existence of a fog during the oxidation of TEL vapour in non-engine apparatus. In view of its considerable importance from the point of view of knock theory, an attempt has been made using a similar technique to establish whether or not a fog is formed inside the engine cylinder. In addition, it was hoped that measurement of the cyclic times of appearance and

disappearance of the fog with different fuels would provide useful information on the early stages of the interaction of the fuel and TEL.

A great deal of development work was devoted to devising a sensitive optical method of detecting a lead fog within the engine cylinder. Fig 20 shows the

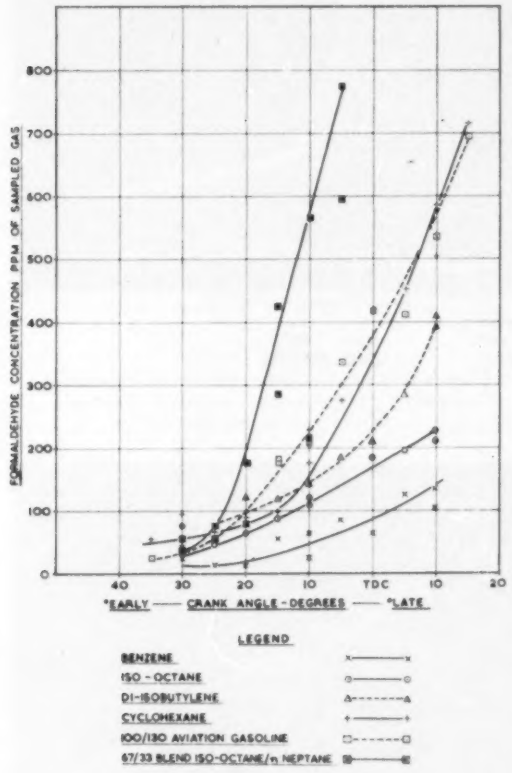


FIG 19

FORMALDEHYDE CONCENTRATION IN GASES SAMPLED FROM THE ENGINE AT VARIOUS CRANK TIMINGS

arrangement finally found to be the best. The light entered the engine cylinder through a quartz window $\frac{1}{8}$ inch in diameter fitted in the combustion chamber wall. The light source, a carbon arc, was focused by a quartz lens at a point approximately 1 inch from the combustion chamber wall. A further quartz window, of 7·5 mm diameter, was lined up on this spot and any light reflected back through this window fell on to a photocell coupled to a cathode ray oscilloscope. The object of the experiment was to detect the presence of a particulate fog by the increase in light reflected back on to the photocell.

To minimize interference due to reflection from fuel droplets, the fuel/air mixture temperature was raised to about 190° C. This did not entirely eliminate the fuel vapour diagram but, by altering the time base sweep to cover 720 crank degrees in one traverse of the CRO tube instead of superimposing two 360° cycles on each other, it was possible to separate out the two effects, since they occurred on different strokes of the engine.

Still further to reduce the importance of light reflection from fuel vapour, a volatile fuel, neohexane, was used for some tests. This gave a very good fog indication with 10 cc/TEL/IG in the fuel (Fig 21 (*a*)). This fuel also gave an intense cool flame, which was picked up by the photomultiplier under these conditions. There seemed in fact to be some sort of relationship between fog indication and cool flame intensity, and benzene, which gives no cool flame, gives only a small fog indication unless the compression ratio of the engine is raised (Fig 21 (*b*)).

Iso-octane + 10 cc TEL/IG gave a good fog indication and of course this fuel has a fairly intense cool flame (Fig 22). It was found possible to detect a fog when the lead concentration was reduced to 5 cc/IG. Fog indications were improved by increasing the compression ratio, but mechanical conditions prevented this being raised above 8·4.

Some experiments were carried out with materials other than TEL to check that the fog indication was due to inorganic lead and not to, say, liquid droplets of TEL. A high-boiling organic compound, ethyl aniline, was added to *iso*-octane in a concentration of 10 cc/IG. This gave no fog indication, suggesting that the fog indication with TEL was unlikely to be due to liquid droplets of TEL. Aryl silicate, when burnt with paraffin in a wick lamp, gave a smoke which, when passed through the engine, resulted in an excellent fog diagram being obtained. Similar indications were obtained using mixed aryl silicates and paraffin separately. A test was also carried out with

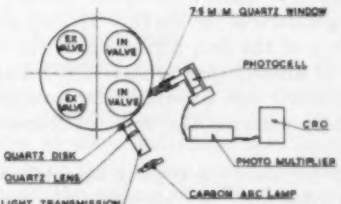


FIG 20

DIAGRAMMATIC LAYOUT OF EQUIPMENT FOR TYNDALL BEAM EXPERIMENTS

ferrocene, added to the fuel in a concentration of 15 g/IG. It was assumed that this would decompose under suitable conditions to give a fog of Fe_2O_3 particles. No fog indication was, however, obtained at this concentration, or even when 30 g/IG were used. Ferrocene was also tested in a carrier fuel which gives

an intense cool flame (50 octane fuel). A high intensity cool flame was obtained but no fog diagram.

It seems almost certain from this evidence that a fog of inorganic lead particles is formed within the engine cylinder near to TDC. The form of the trace of light reflection against crank angle is, however, very extremely difficult. In view of this it was decided to discontinue the Tyndall beam work at this stage.

It might be mentioned that the times of first appearance of the lead fog noted above, 70° to 80° before TDC, are by no means inconsistent with the timings of early decomposition of the TEL obtained

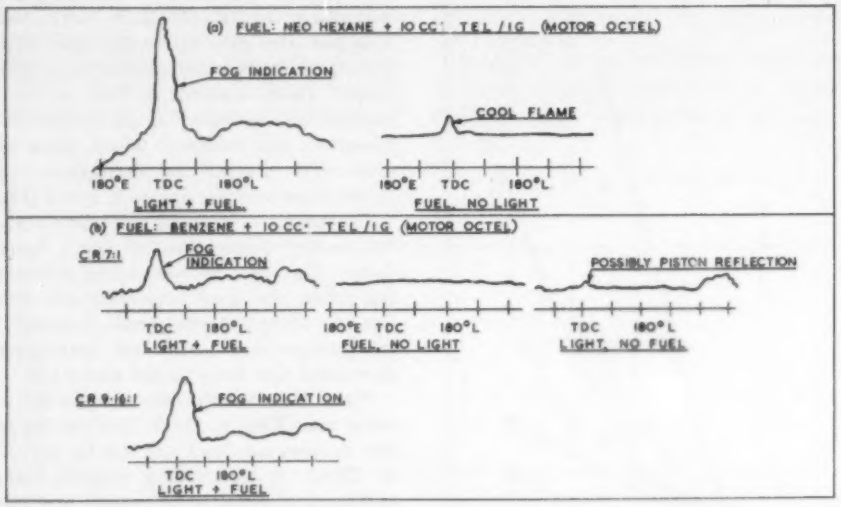


FIG 21

TYNDALL BEAM EXPERIMENTS—TYPICAL CRO DIAGRAMS

much influenced by compression due to the piston. Peak fog intensity is observed at TDC because the particles have been compressed into the smallest volume at that time. The fog appears to be first formed at around 90° before TDC, but the exact time of formation is difficult to detect visually because of the rising nature of the curve. To help decide on the exact time of the first formation of the fog, a large number of photographs of these CRO diagrams have been obtained and examined for common features which may indicate the time of formation of the lead fog.

Fig 23 (*a*) shows a typical example of the CRO diagram obtained. In all cases the trace sharply increased between 70° and 80° before TDC and, in order to link this more positively with the time of lead fog formation, some further photographs were obtained at a lower compression ratio, where it might be expected that the fog would be formed later in the cycle. It was found, however, that under these conditions the fog indication became less distinct and it was more difficult to decide the exact time at which the trace turned sharply up (Fig 23 (*b*)). It was evident that the tests were being carried out at the limit of detection of the lead fog, and any condition which decreased the sensitivity made identification

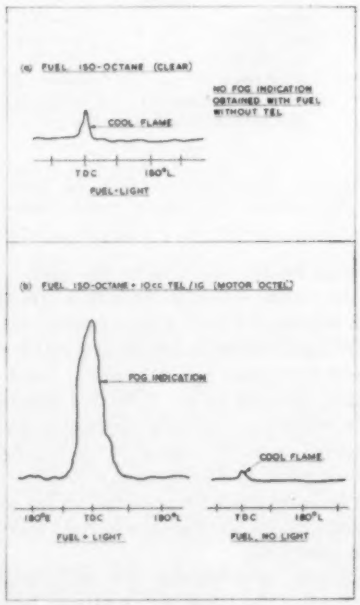


FIG 22

TYNDALL BEAM EXPERIMENTS—TYPICAL CRO DIAGRAMS

from the lead sampling experiments, 30° to 40° before TDC. It has to be remembered that the Tyndall beam experiments were carried out at high compression ratios and at high intake air temperatures,

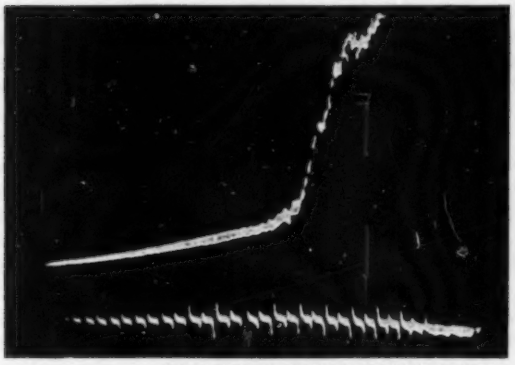
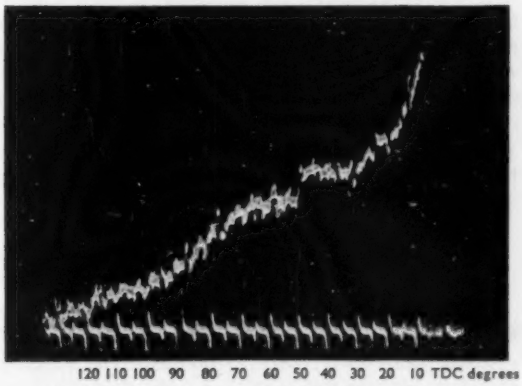


FIG 23

TYNDALL BEAM EXPERIMENTS—CRO DIAGRAMS

(*a*) Fuel: *iso*-octane +40 cc TEL/IG. CR 9·4
Mixture temperature 112° C



(*b*) Fuel: *iso*-octane +40 cc TEL/IG. CR 8·05
Mixture temperature 90° C

both of which factors would give earlier TEL decomposition.

DISCUSSION

A method has been developed for following the decomposition of TEL from the organic to the inorganic form in the end-gas of a fired engine. It was at once obvious that, under given engine operating conditions, there were big differences between the fuels in the timing and shape of the TEL decomposition curves. Taking the pure fuels first, benzene, and particularly methanol, had markedly later TEL decomposition curves than the other fuels. This would appear to support the idea that the pre-reaction of the fuel plays some part on TEL decomposition, as both fuels are known to give little or no pre-reaction before combustion and no cool flame. The high latent head of methanol, which calculation shows to result in an end-gas temperature of 600° C being reached only at 2·5° after TDC, whereas with *iso*-octane, for instance, it is reached 17·5° earlier, is clearly also a contributing factor.

The curve with di-*iso*butylene, which is also later than that for *iso*-octane, similarly accords with the suggested correlation between lead decomposition and the tendency of the fuel to give pre-reactions. It is curious, however, that the curve with the 67/33 blend of *iso*-octane and heptane is also slightly later, whereas the reverse would be expected from their known relative reactivities, and this reverse result has in fact been observed by Rifkin and Walcutt in similar engine experiments.[10] The decomposition of TEL with *cyclo*hexane appears to start earlier in the cycle than with any other fuel, but to continue at a much slower rate, so that the TEL is not completely decomposed to the inorganic form until nearly the arrival of the flame. No explanation of this phenomenon has yet been put forward.

It is interesting that although there is such a big difference between the TEL decomposition of, say, benzene and of *iso*-octane at a low compression ratio, when the compression ratios are raised so as to be near the knock limit for each particular fuel, the TEL decomposition curve for benzene advances considerably, whereas that for *iso*-octane remains virtually unchanged. At these higher compression ratios, which are after all those at which the TEL has to exert its anti-knock effect, the TEL decomposition is not markedly later in benzene than in some other fuels, so it might be said that benzene is as well prepared as the other fuels, and therefore its lack of effectiveness must reside not in the preparational stage, but in the subsequent inhibiting stage, as surmised in the introduction.

Further interesting evidence relating to benzene and methanol is presented by the tests in which additions of diethyl ether were made to the fuels. The addition of ether had favourable effects on the lead response of both fuels, gave weak cool flames, and advanced the timing of TEL decomposition in the case of methanol, but not of benzene.

The effect of intake air heat on TEL decomposition is in accord with expectations, the higher the intake air heat, the earlier the TEL decomposition. It has also been shown that the higher the intake heat, the lower the lead response. It may be, therefore, that there is an optimum time in the cycle for TEL to decompose in order to exert its maximum effect, and this time could be different for different fuels. It is possible that, in these tests, the optimum has been exceeded in the case of the tests at the higher intake air heat and that the TEL decomposes too early in

the cycle for maximum effectiveness. Alternatively, it might be suggested that the higher intake air heat affects the course of the pre-flame reactions in such a way as to make them less susceptible to inhibition by TEL.

There has been shown to be a broad relation between TEL decomposition at a compression ratio of 5·0 and the knock-limited compression ratio of clear fuel, but whether this has any significance so far as lead response is concerned may be doubted, as there seems to be no similar relation when the compression ratio near to the knock limit is considered. It is also broadly true that the earlier the decomposition of the TEL, the better the lead response, but the scatter of observations is so great that it is clear that some other factor must also be involved.

There seems no simple relation between the motored engine figures and TEL decomposition. It is true that there is a relation between the 50 per cent TEL decomposition point and the hot flame limit of the clear fuel, but this would in any case have been expected to follow from the similar relation with the knock limited compression ratio. It is clear that if the cool flame has an influence on TEL decomposition, some other factor must be involved in addition. It is probable that cool flame intensity should not be considered in isolation from other factors when deciding its influence on TEL decomposition. Rifkin and Walcutt [10] have suggested that temperature has the primary influence on TEL decomposition. A fuel of high anti-knock value which is going to utilize its TEL at a high compression ratio has, therefore, an advantage, because the compression of the fuel/air mixture by the piston will be sufficient to heat the TEL to a high value. Such a fuel may, therefore, need a cool flame of much lower intensity finally to decompose the TEL than a fuel of lower knock-rating which requires its anti-knock effect at lower compression ratios, where the temperature rise due to compression by the piston will be much less. It is probable, therefore, that it is total temperature rise, by adiabatic compression, by pre-cool flame reactions, and by the cool flame itself which is important and which should be considered in an investigation of this sort. Unfortunately, these vital temperature rises are taking place in the fired engine in only a small part of the charge, the end-gas, and during a period of steeply rising temperature and pressure. Our measurements and estimates of temperatures under these conditions are not sufficiently accurate to permit clear conclusions to be drawn. The only way to obtain such figures would be by use of a motored engine for TEL decomposition measurements, and the conditions of residuals, etc., are sufficiently different in a motored engine from a fired engine to make one regard this as less than the ideal.

The formaldehyde concentration curves suggest that for those fuels which form one, the timing of the cool flame is right for having an influence on TEL decomposition.

Aviation Octel and Motor Octel seemed to retard the decomposition of the TEL by about the same amount as compared with pure TEL. This is an interesting result, as it has repeatedly been observed that with the TEL concentrations now being considered, the ethylene dichloride and ethylene dibromide added in TEL mixes have virtually no effect on the anti-knock effectiveness of the TEL.

On the other hand, two well-known sulphur-containing anti-knock antagonists were tested and they were found to behave in very different ways. Di-tertiary butyl tetrasulphide acted early in the cycle and markedly advanced the TEL decomposition curve. Butyl mercaptan, however, had virtually no effect on either the timing or rate of TEL decomposition. It is evident that di-tertiary butyl tetrasulphide exerts its lead antagonistic effect on the preparational stage of lead anti-knock action and converts the TEL to lead sulphide rather than to the more effective lead oxide. Butyl mercaptan must act at a later stage, perhaps by poisoning the fog of PbO particles.

Finally, so far as lead itself is concerned, the Tyndall beam experiments would appear to demonstrate without doubt the existence of an inorganic lead fog within the engine cylinder. The time of first formation of this fog has not been determined with any exactitude. Neither has it been possible to determine the effect of fuel type on fog formation, except for the suggestion of a very general relationship with cool flame intensity. It is clear, however, that the fog is formed in ample time to exert an influence on the course of the pre-knock chemical reactions.

CONCLUSIONS

This programme of work, by demonstrating that a fog of inorganic lead particles is formed in the engine cylinder sufficiently early to influence the chemical reactions leading to knock, not only sheds valuable light on the mode of anti-knock action of TEL but also confirms the importance of the study of the mechanism of formation of the inorganic particles from the original organic TEL.

This investigation has shown that fuel type has an important influence on the decomposition of TEL from the organic to the inorganic phase. Under fixed engine conditions it seems generally true that the higher the knock rating of the fuel, the later the TEL decomposition. In particular, it would appear from the timings of cool flame formation and of TEL decomposition that the cool flame plays some part in decomposing the TEL to the active form. There would not, however, appear to be a very close relationship between TEL decomposition and cool flame intensity, and it would seem probable that the influence of the cool flame should not be considered in

isolation from the other factors, such as pre-cool flame oxidation and adiabatic compression, which contribute to the overall temperature rise in the end-gas at the time of TEL decomposition.

It is significant, too, that when the severity of the engine operating conditions is increased, by raising the compression ratio to the knock limit in all cases, the TEL decomposition is advanced to a sufficiently early timing to ensure the presence of a lead fog during the knocking reactions, even with fuels of poor lead response, such as benzene and methanol. Even the addition of ether to these fuels, which increased their cool flame intensities and their lead response, had no effect on the timing of TEL decomposition with benzene and only a small effect with methanol.

Thus, while it is broadly true that the earlier the decomposition of the TEL, the better the lead response of the fuel, the scatter of results is sufficiently great to suggest that this is by no means the only factor involved. The observations of the effect of intake air temperature on lead response and on TEL decomposition with di-*iso*butylene as fuel would not support the idea of a very close relation between the two.

In conclusion, therefore, this investigation would appear to show that of the two stages into which the anti-knock activity of TEL might be divided, the preparational and the inhibiting, it is the latter which is probably the more important. It is proposed to discuss this latter aspect of the anti-knock activity of lead in a later paper.

ACKNOWLEDGMENTS

This work was carried out in the laboratory of Ricardo & Co. Engineers (1927) Ltd, on behalf of The Associated Ethyl Co. Ltd. The authors are indebted to both these companies for permission to publish this paper. They also acknowledge generous help from Shell International Petroleum Co. Ltd in providing samples of fuels and chemicals and assistance in some of the analytical work.

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APPENDIX

THE DETERMINATION OF ORGANIC AND INORGANIC LEAD

At the termination of an engine run the contents of the various traps in the absorption train were treated as follows:

Aqueous Layer, Hydrazine Hydrate Solution, Iodine Solution, and Nitric Acid Washings

Each solution (except the iodine solution) was treated with aqua regia, followed by evaporation (including the iodine solution) to small volume. Perchloric acid (60 per cent w/w) was added (except to the iodine solution), and the solutions evaporated to dryness. The residues were dissolved in hot dilute hydrochloric acid, and hydroxylamine hydrochloride (5 per cent w/v) added, in order to prevent subsequent polarographic interference of iron. The solutions were transferred to standard volumetric flasks, and made up to volume with distilled water after the addition of gelatin (0·05 per cent w/v) as a maximum suppressor aid.

Nickel Foil

The nickel foil was cut into small pieces and left in contact with dilute aqua regia for five minutes. The solution was decanted and then prepared for polarographic treatment, as outlined previously.

Hydrocarbon Layer

The hydrocarbon layer was treated with a solution of bromine in carbon tetrachloride (30 per cent bromine by vol) in order to decompose the TEL. The lead salts thus formed were extracted with dilute nitric acid, and the solution evaporated to small volume, and then prepared for polarographic treatment, as outlined above.

Glass Wool Trap

The glass wool was extracted with benzene in a Soxhlet apparatus, in order to remove any undecomposed TEL. The benzene extract was treated in a similar manner to the hydrocarbon layer.

The inorganic lead remaining in the glass wool was removed by refluxing with nitric acid (sp gr 1·42) and evaporated to small volume. The solution was then treated in the manner outlined previously.

Polarographic Determination

Standard lead solutions were prepared from reagent quality lead nitrate crystals, and these were used to calibrate the recording polarograph. All reagents used in these test methods were checked for lead content.

All the samples were recorded between −0·2 v and −0·9 v and compared with the standard polarograms.

DISCUSSION

J. R. Lodwick (The British Petroleum Co. Ltd): The authors have presented an interesting paper which contributes to the fuller understanding of the circumstances governing knock in engines and of the way TEL functions as an anti-knock additive. In our eagerness to discuss the theoretical implications of the paper, however, we must not overlook the ingenuity with which the various experiments were planned and carried out.

Some 40 years have passed since such workers as Ricardo, Kettering, Midgley, and Boyd recognized that "knock" in spark-ignition engines was a critical factor in limiting the efficiency and power output of these

engines. Much research has been carried out in the intervening years and has resulted in the modern, high-compression spark-ignition engine of enhanced efficiency operating on fuels of high knock resistance.

We have not yet reached optimum CR, however, and it would appear that manifestations of surface ignition described as "rumble," "thud," or "wild ping" must be met and overcome before optimum efficiency is achieved. Many present here and concerned with this problem will be heartened by the appearance of this paper written in terms of more basic principles than those of ON, manifold pressure, ignition setting, etc.

Turning first to the results of TEL decomposition in the fired E35 engine, the results on the 67/33 *iso*-octane/*n*-heptane blend appear to be out of line not only with the Rifkin and Walcutt results,[1] but are also inconsistent with the level of formaldehyde development given by this blend as compared with *iso*-octane (see Fig 19). The results are also inconsistent with the knowledge that the lead response of such a blend is significantly greater than that for *iso*-octane. Can the authors comment on these further observations and have they any data available on the behaviour of *n*-heptane in the fired engine which could dispose of this apparent anomaly?

Rifkin and Walcutt, in other work,[2,3] have indicated that the existence of pre-combustion reactions (the preparational stage) can induce greater TEL effectiveness, probably by giving higher temperatures and thus greater TEL decomposition. They are also in agreement with the authors in believing that TEL must decompose to give the vital anti-knock species. They suggest that a temperature of at least 700° F must be achieved to give appreciable decomposition. This decomposition of TEL is affected by temperature and time only; it is affected by fuel type in as much as fuels vary in the amount of their exothermic pre-flame reactions (the preparational stage) which contribute to charge temperature. That TEL exhibits anti-knock action only when thermally decomposed was shown very convincingly by carrying out motored engine experiments in which 50 ON primary reference fuel was made to show no TEL response. This experiment was based on the fact that TEL decomposition is affected by temperature but not by pressure, whereas the ignition delay of the fuel–air mix is dependent on both temperature and pressure. By increasing manifold pressure and compression ratio the auto-ignition temperature of the charge was lowered to a point below the decomposition temperature of TEL, and in these circumstances no anti-knock action was displayed. The authors' comments on these results would be welcomed.

Perhaps a question on the much-debated character of the active species which gives TEL its anti-knock action, and which the authors believe to be a fog of PbO, would not be amiss. I wonder if they have any evidence as to the size of the PbO particles? It has been suggested that this might have some bearing on the efficiency of the anti-knock reaction. Perhaps, for example, the action of the preparational stage products may have some effect on the state or division or exact chemical composition of this fog.

There are many questions which could be answered by an extension of the work described this evening. Perhaps the authors or some of the other speakers might care to comment on some of them. They are:

1. Are the different decomposition rates of TML and TEL likely to give rise to any significant differences in engine performance?

2. Are there any likely explanations as to the role played by tertiary butyl acetate as a lead appreciator?

3. TEL is not very effective when used as an anti-knock in diolefins, acetylenes, unsaturated bicyclics, and in some cases, for example, with di*cyclo*pentadiene, 1,3-*cyclo*pentadiene, 2-methy[1]-1,3-butadiene, it acts as a knock inducer. What explanation, if any, can be offered for this tendency to induce knock?

In conclusion I should like to thank the authors for their very stimulating paper. Continued work in this field supported by studies on the oxidation of hydrocarbons and the use of gas–liquid chromatography should lead to a fuller understanding of present and future problems.

S. T. Griffiths: Our TEL decomposition results, obtained with the 67/33 blend of *iso*-octane and *n*-heptane, are not in accord with our expectations. We find it very difficult to provide an explanation. It will be recalled, however, that our TEL decomposition data was obtained with this blend at 5 : 1 CR, and the TEL decomposition with *iso*-octane was obtained at 5 : 1 and also at a higher CR. It would seem to me a very interesting experiment if we were to increase the CR and obtain TEL decomposition curves with 67/33, although the amount by which we could increase the CR would undoubtedly be limited, due to the relatively low ON of this fuel. As Mr Lodwick points out, our formaldehyde curves are in accord with the lead response data, and it is the TEL decomposition data that are apparently out of line.

Concerning the remarks on a similar type of work which has been carried out by Rifkin and Walcutt, I think that, generally, their results and ours are in good agreement. Mr Lodwick mentioned that a temperature of at least 700° F is required for the decomposition of TEL, and from our calculations of end gas temperature this is similar to the values we obtained. We provided an example in the paper with *iso*-octane at 15° before tdc. We calculated the end gas temperature to be 1110° F, which we obtained by use of the gas laws, etc. This is at 15° before tdc, when the major portion of TEL decomposition has occurred, so the temperature for incipient TEL decomposition would be considerably lower than this, at, say, 40° before tdc.

We have not determined the size of lead fog particles, but Rifkin has done this and has reported particle sizes between 15 and 500 Å. There is a distribution pattern between these two extremes. It is felt that the size of the lead fog particles is very important and, in fact, our thoughts are that if these particles agglomerate and grow in size, they probably become less effective for destroying chain carriers on their surface.

On the question concerning TML and TEL, it seems to me that the decomposition of TML, owing to its greater thermal stability, would occur later in the combustion cycle than the decomposition of TEL. Mr Lodwick questioned whether such a difference leads to perhaps a difference in engine performance. I think it does and will endeavour to give an example. In a CFR Research engine, where we can eliminate the effect of fuel segregation factors, it is found that the lead response of TML and TEL, shall we say, with a catalytically reformed fuel is rather similar at the equivalent of 3·0 ml TEL/U.S. gal. However, at half this lead concentration (and, therefore,

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at less severe engine conditions) it is usually found that the lead response of TEL is superior to that of TML, and this seems to indicate that whilst the general anti-knock action of the two lead compounds is similar, it differs in detail.

Further, I could add that it is now well known that TML looks somewhat better when rated by the CFR Motor Method than by the CFR Research Method. It will be recalled that the temperature of the intake air is higher with the motor engine than it is with the research engine. It would follow that this increase in engine severity advances the cyclic timing of TML decomposition to a position nearer to the optimum decomposition timing, yet possibly in retard of it. Under similar conditions, the cyclic timing for TEL decomposition would still be in advance of TML decomposition, and also possibly somewhat in advance of the optimum value. Since TML decomposition occurs later in the combustion cycle than TEL decomposition, and both decompositions must be completed by flame arrival, it would seem that TML lead decomposition must be carried out at a faster rate.

The next question concerned the beneficial effect of *t*-butyl acetate on TEL. We have done quite a number of experiments with *t*-butyl acetate and find that, in certain circumstances, it has a beneficial effect on the lead response of certain fuels. The beneficial effect increases with TEL content. As to likely explanations why this should happen, I will restrain myself to giving a possible two!

I have said earlier that the size of the lead fog particles is very important, and it may be that *t*-butyl acetate delays the agglomeration of the lead oxide particles to form larger particles, which would be less effective in the end gas. A second mode of operation could be that the lead oxide fog particles, when they have caused destruction of the chain carriers on their surfaces, may become de-activated. Perhaps *t*-butyl acetate reactivates these lead oxide particles.

Of these two explanations, I think perhaps the former is the one I prefer.

Attention is then drawn to the fact that TEL is a knock inducer in a fuel such as di*cyclo*pentadiene. As I have shown, TEL is also a knock inducer in benzene in certain engine conditions. This, it is felt, is because TEL is the vehicle in which the active ingredient is contained, and unfortunately this vehicle has to be hydrocarbon in nature. In other words, the four ethyl groups attached to the central lead atom, in certain circumstances, such as the ignition of benzene, cause premature knock.

J. H. Boddy (Mobil Oil Co. Ltd): Fig 13 seems to me to be very significant. It shows that the timing for 50 per cent decomposition of TEL is constant, irrespective of the knock-limiting CR of the fuel. I wondered whether Mr Griffiths could endeavour to give some sort of temperature and pressure significance to those points, rather than just crank angle timing. It would possibly point to the fact that the TEL decomposition is associated with physical conditions pertaining in the cylinder, rather than any chemical stimulus of the fuel on the decomposition.

I would also like further classification of Mr Griffiths' answer to Mr Lodwick concerning TML. The evidence of octane testing in single-cylinder engines is that TML is less effective than TEL at low concentrations, but that TML catches up and overtakes TEL at high concentrations of lead. Mr Griffiths stated that TML decomposed more rapidly than TEL. Would he confirm that this is so? Admittedly it is more volatile, but this does not necessarily indicate that it is more readily decomposed. Would he please go over his explanations again as to why TML is less effective in low concentrations?

S. T. Griffiths: On the question concerning Fig 13, we find at these higher CR that the timing for 50 per cent TEL decomposition is in fact roughly constant, although there is some scatter between the points. I think possibly you are right in suggesting that the temperature at these particular crank angle timings is constant for the individual fuels that we have examined. We cannot say this for certain, although this possibility was explored, but unfortunately the calculation of end gas temperature is extremely difficult, either using the gas laws or reaction kinetics. It was decided that we would not present our temperature measurements at this meeting on account of the lack of accuracy in determining them.

I have a suspicion that Mr Boddy may be right in that these points may be similarly related with respect to end gas temperature.

Repeating what I said about TEL and TML effectiveness in a single cylinder engine, in a single cylinder engine, where there is no fuel anti-knock segregation, and taking a catalytic reformate as an example, at the equivalent concentration of 3 ml/U.S. gal, it is found generally that the lead response is similar for TML and TEL. At half this concentration, 1·5 ml TEL/U.S. gal, it is found that TEL has a superiority in lead response over TML, and I suggest that the mode of anti-knock action of TEL and TML is generally similar, but differs, obviously, in detail.

Perhaps what caused a little confusion is this concept of rate of decomposition. I will try to explain this a little further. TML is more resistant to decomposition than is TEL and, therefore, decomposes later in the combustion cycle. Once decomposition occurs it must be completed by flame arrival within the combustion chamber. Therefore, on the one hand it is more resistant to decomposition, and on the other hand its subsequent rate of decomposition (by definition if preferred) is likely to be faster, since it must be completed by flame arrival.

G. A. Dickins (Mobil Oil Co. Ltd): We all put other additives in our gasoline, for various reasons. Sometimes we put in phosphates and I would like to know of any effects these materials may have on the various decomposition processes that Mr Griffiths has been describing. If so, is anything known about the mechanism of that process?

S. T. Griffiths: Unfortunately the answer is that we have not investigated the effect of phosphorus compounds on the decomposition of TEL. However, if I may give an opinion on this, which is not coupled with experimental fact, it would seem to me that a phosphorus compound would possibly behave in a similar manner to a sulphur compound. Some of the phosphorus compounds are known to be lead antagonists, and some are not. I would suggest that the ones which do have a lead antagonistic effect probably derive this either from the preparational stage or the subsequent inhibiting stage. It has been shown that sulphur can behave in both ways, depending on the sulphur compound taken. Therefore, if the organic phosphorus compound was in fact a lead antagonist, I would expect that it could do one of two things: it could affect the preparational stage or it could affect the subsequent inhibiting stage.

D. H. Desty (The British Petroleum Co. Ltd): I wonder if the authors would care to comment on whether

the anomalous results obtained with *cyclo*hexane (see Fig 4) are in any way associated with its poor performance under conditions where heterogeneous combustion becomes significant.

Secondly, as this hydrocarbon has been shown to give anomalous results, why was it chosen to explore the effect of added sulphur compounds?

D. Downs: We do not know why *cyclo*hexane behaves in the way shown in Fig 4. *cyclo*Hexane was chosen for investigation as a representative of the naphthenic group, and the TEL decomposition curve obtained on this fuel is well established, containing a number of check points, not all of which are shown on Fig 4. Thus there would seem to be no doubt about the result, but we cannot explain it.

Our choice of *cyclo*hexane as a base fuel for the investigation of the addition of sulphur compounds was dictated largely by fuel availability, and also by the fact that the TEL decomposition curve with *cyclo*hexane as fuel was so well established.

D. H. Desty: Were any attempts made to keep the internal condition of the engine surfaces reasonably constant? In other words, were the deposits cleaned out regularly? Presumably this might be some explanation of the *cyclo*hexane effect.

D. Downs: The internal surfaces of the combustion chamber remained remarkably clean throughout the test period, probably due to the fact that we operated under continuous full load conditions, and also because the lubricating oil consumption of the engine was very low. We found, in fact, that there was very little difference in TEL decomposition: (1) with a clean engine; and (2) with an engine nearing its time for cleaning, after some 60–70 hours operation.

J. H. Boddy: Could I ask a question concerning the reproducibility of the curve which the authors obtained on any one fuel? Did they make any correction of changes of atmosphere conditions, or were the effects of these changes insignificant?

D. Downs: I think that a good example of reproducibility is shown on Figs 6 and 7. We carried out first the series of tests shown on Fig 6, which compares the TEL decomposition with pure TEL and with aviation octel, and were frankly surprised at the result. As the anti-knock actions of pure TEL and of aviation octel are virtually the same, we had not expected that there would be any difference between them in TEL decomposition, yet this curve shows TEL decomposition occurring some eight crank degrees earlier with pure TEL than with aviation octel.

We repeated the test series, but as we had exhausted our supplies of base fuel, we had to use another batch which, however, was of virtually the same composition. We also added motor octel to the test series. The results of this second test series are shown in Fig 7, and if one compares Fig 7 with Fig 6 it will be seen that there are detailed differences between the curves, but the general comparison between pure TEL and aviation octel has been repeated to a quite remarkable degree considering the length of time which elapsed between these two series of tests.

Another indication of the repeatability of the results is given in Fig 3. This figure was, in fact, built up over a long period of time, tests 316–320 being obtained at one time and tests 356 and 369 at widely-spaced times afterwards. Yet all these points lie on a good curve, and this is representative of the repeatability obtained.

It is this sort of repeatability which makes it difficult to ignore apparent anomalies, such as the comparison between *iso*-octane and the 67/33 blend of *iso*-octane and *n*-heptane.

H. C. Rampton (The British Petroleum Co. Ltd): As a chemist, could I ask if, in view of the curious result obtained with *cyclo*hexane, you would expect the same anomaly to occur using methyl *cyclo*pentane and what effect would *cyclo*hexane have?

R. W. Wheeler: We did not obtain any lead decomposition data on either of these fuels.

We would have liked to investigate this effect with *cyclo*hexane further, but time and the non-availability of such fuels as you mentioned prevented this.

J. R. Lodwick: The possibility was mentioned of measuring temperatures, or the difficulty of measuring temperatures in the end gas. I think I read somewhere that there had been a method developed based on measurement of the speed of sound in the end gas, and then calculating to give the temperature. I wondered whether Mr Downs could comment on the possibility of using this technique. It would seem that to establish the temperatures with reasonable accuracy would help the theory a little further.

D. Downs: I have not had experience with that technique, and I think the difficulty is to obtain sight of a sufficient length of end gas under constant conditions to enable measurements to be made. Towards the end of the pre-flame process the end gas is spread over a very thin arc, and temperature conditions must vary considerably within this arc.

If one wants to relate events in the cylinder more closely to the temperature and pressure conditions obtaining—and this is naturally what a chemist would want to do—one must, as Rifkin did, go to a motored engine. With the motored engine, calculations can be more accurate and one would have a better chance of using experimental techniques, such as the measurement of the speed of sound in gases.

Dr E. B. Evans (Esso Research Ltd): There is, I believe, a little difference of opinion existing with regard to the relative role played by lead and the oxides in the anti-knock process. Presumably, in the thermal decomposition of TEL, the first product is metallic lead, subsequently oxidizing to the oxide, and perhaps getting the oxygen from the active products forms from the initial oxidation of hydrocarbon molecules. Is there any suggestion from the results obtained that the oxidation of the initial lead to the oxide plays any part at all in the inhibitive action or in the preparational stage, or is that obscured by the conditions?

There is one other point, which would perhaps be interesting to investigate, and that is the effect of a scavenging agent which would decompose at a low temperature. Ethylene dichloride and ethylene dibromide do not begin to decompose thermally at any considerable rate below temperatures of about 400° C, whereas TEL decomposes at about 200° C. If one used a scavenging agent which decomposed readily at low temperatures, what sort of effects would one expect to observe in a series of experiments such as those carried out? Have you tried any scavenging agent apart from the conventional ethylene dihalides?

S. T. Griffiths: We have not obtained any direct information from these experiments to indicate whether TEL first decomposes to metallic lead, and then oxidizes, to lead oxide. In fact, in our experiments, we are limited to observing inorganic lead compounds and in our Tyndall Beam experiments we have deliberately written that this fog is a fog of inorganic lead particles, because we cannot be more specific, using this technique. We feel rather sure that they are lead oxide particles, but in fact our Tyndall Beam experiments only give us an indication of light reflection from smoke particles.

I should point out that whilst the decomposition temperature given for TEL in the open literature is 200° C, this, of course, is under ambient pressure conditions, and in the end gas of the engine it is occurring at a much higher temperature.

R. W. Wheeler: Dr Evans asked if we had any evidence that the oxidation of the initial lead to the oxide plays any part in the inhibition. We have no direct evidence, and indeed it may be possible that lead is not formed at all. The TEL may first oxidize to an ethoxide which finally decomposes to PbO. Such reactions are known in other metal alkyls, such as zinc diethyl.

Dr E. B. Evans: Presumably, then, the oxygen will also come from the active centres?

R. W. Wheeler: It could do.

Dr E. B. Evans: The partly oxidized hydrocarbons?

R. W. Wheeler: It could come from them. It was one of the hypotheses we worked on. It may come from oxygen in the cool flame products.

Dr E. B. Evans: It depends whether the cool flame precedes the decomposition, or the other way round?

R. W. Wheeler: Yes. Another indication that our fog was of lead oxide was provided by the fact that ferrocene gave no fog indication, presumably because the reddish-brown iron oxide formed could not be observed by our blue-green sensitive photomultiplier tube, whereas yellow-white PbO would be readily detected. A fog of lead itself would probably be of dark grey colour. The fact that we readily detected the light scattered by the fog over the parts of the cycle where lead must exert its effect points to its being PbO.

D. H. Desty: As a mere chemist, it is with some diffidence that I make the suggestion that it might be interesting to do this kind of work, not in an engine, in view of the difficulties we have been discussing, in sampling, temperature measurement, and following the various active species which occur in this kind of work. I would appreciate the comments of the authors on the possibility of doing investigations of this type in apparatus in which the combustion of the hydrocarbon mixture is conducted as a steady state, the two stages of combustion occurring in separate zones of the apparatus.

S. T. Griffiths: I think that a combination of engine experiments coupled with non-engine experiments is essential, and this is the type of attack we have had on this problem. My opinion is that one should always do both, because I feel that if one does only the non-engine experiment one may be misled, and there are difficulties the other way round.

D. Downs: I agree with Mr Griffiths on this point. Much of the early work relating to combustion in engines was bedevilled by the fact that it was done under non-engine conditions where it is impossible to reproduce exactly the conditions of an engine. The continuous flow type of experiment, mentioned by Mr Desty, is normally carried out at low pressures. It is very difficult to carry out this type of experiment under the high pressure conditions obtaining in an engine.

With a simple laboratory apparatus it is very easy to get a large number of results on, say, oxidation rate in a comparatively short time. This probably has little relevance, however, to what is going on inside an engine under very different conditions of temperature, pressure, and time. If one tries to modify the laboratory apparatus to bring it more into line with the engine the apparatus becomes more and more like an engine. So why not start with an engine in the first place?

The Chairman then proposed a vote of thanks to the authors, which was accorded with acclamation.

THE WETTING OF "AIR-DRY" STONE BY BITUMINOUS BINDERS IN THE ROAD SURFACE DRESSING OPERATION *

By E. J. DICKINSON †

SUMMARY

Factors affecting the retention of stone on a surface dressing laid under dry conditions on a lightly trafficked road carrying fast traffic have been investigated.

To ensure permanent retention of stone two of the conditions that must be fulfilled are:

(1) The surface viscosity of the sprayed binder film must be sufficiently low to enable the stone to be rapidly wetted.

(2) The binder film must have a sufficiently low viscosity during the 24-hour period following application so that pneumatic-tyred traffic can arrange the stone in the form of an inter-locking mosaic.

Under the settled weather conditions often prevailing in the inland regions of the Union of South Africa, the road surface temperature shows a regular daily variation, and the road surface temperature at sunrise can be used to predict the temperature conditions during the next 24 hours. Consequently, this temperature can be used as a guide to the choice of grade of binder to ensure complete retention of the stone chippings.

"Cutback" bitumens, although suitable for surface dressing under cold conditions, are not so effective as would be expected from their low bulk viscosity, because evaporation of oil from the top of the sprayed binder film gives an increase in surface viscosity. Crude source of a bitumen does not appear to have an important effect on wetting properties for air-dry roadstone, and neither addition of long-chain polymers, soluble fatty acids and esters, nor cationic wetting agents effects any significant improvement in wetting properties under dry conditions.

Dust on the surface of the stone retards wetting, but the mineral composition of the stone does not appear to have an important effect on the process.

INTRODUCTION

A LARGE proportion of the bituminous road surfacings in the Union of South Africa is constructed and maintained by the surface dressing method of spraying a film of binder on to the road and covering this with stone chippings. These chippings are most often applied in the "air-dry" state or rapidly attain this state by evaporation of surface moisture after spreading. Invariably there is a film of dust strongly adhering to the surface of the chippings, and often loose dust is present as well.

The investigations described in this paper deal with some aspects of the factors affecting the attainment of adhesion between a bituminous binder and chippings in such a condition, and also with other factors necessary for the production of a durable surface dressing under the fast but light traffic conditions which occur on many of the rural roads in the country.

Previously investigators have paid little or no attention to this problem, but have concentrated on finding ways and means of obtaining adhesion when the stone remains in a moist or wet condition after application to the binder film. Mathews has given a survey of present knowledge regarding the general problem of adhesion in bituminous road materials,[1] and more recently has written a general paper on the adhesion of bituminous binders to road aggregates.[2] Apart from general observations on the effect of dust and the importance of binder viscosity in the process of wetting an aggregate, there appears to be little information on the factors affecting the adhesion of a binder to "air-dry" roadstone. The problem is usually more important in a resealing operation than in the construction of a new surfacing. With the former, a single surface dressing is usually applied and traffic is allowed on to the work soon after its completion. With the latter, several dressings are applied, and often the surfacing does not receive traffic for a considerable time after it is completed.

Among the factors governing the successful resealing of a bituminous road using "air-dry" stone, the following are known to be important:

(1) Choice of the appropriate grade of binder for the prevailing weather conditions.

(2) Choice of the correct thickness of binder film in relation to the size of stone being used and the condition of the old road surface.

(3) Application of the binder as an even film over the road surface.

(4) Use of a "single-sized" stone as free as possible from dust and of size appropriate to the traffic conditions and the condition of the old road surface.

Hitherto the choice of binder grade in relation to weather conditions has been based on experience,

* MS received 4 August 1960.

† National Institute for Road Research, South African Council for Scientific and Industrial Research.

different grades being recommended for different seasons of the year. There has been no guide to choice of binder grade in relation to the actual road conditions at the time of laying. Before investigating the behaviour of single surface dressings laid under different weather conditions, a preliminary examination was made of the condition of a binder immediately after spraying on to the road, and data on road surface temperature conditions for sites near Pretoria were analysed.

A. CONDITION OF A BINDER IMMEDIATELY AFTER SPRAYING ON TO THE ROAD

When a hot binder is sprayed on to the road it rapidly reaches the road surface temperature. Fig 1 shows the change in temperature (measured with a thermocouple) of a binder film from the instant of application and also the associated change in (bulk) viscosity. Two minutes after contact with the road the binder is at the road temperature. As a consequence, the viscosity at which the binder is brought into contact with the stone chip is, to a first approximation, the viscosity of the binder at the temperature of the road surface despite the fact that it has been sprayed at a high temperature. A consequence of this rapid cooling of the sprayed binder is that a negligible increase in binder viscosity takes place on spraying. Williams [3] found that a 32 EVT tar sprayed at 280° F on to a polythene membrane spread on to the road and immediately recovered from the membrane by hot centrifuging increased in EVT by only 1° C.

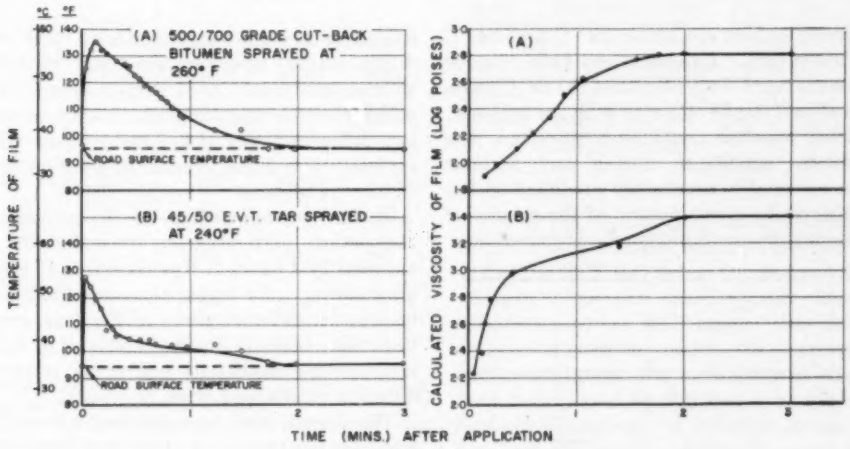

FIG 1

CHANGE IN TEMPERATURE AND ASSOCIATED CHANGE IN BULK VISCOSITY (CALCULATED) OF BINDER FILMS WHEN SPRAYED ON TO THE ROAD

B. DAILY AND SEASONAL CHANGES IN ROAD TEMPERATURE CONDITIONS IN THE INLAND REGIONS OF THE UNION OF SOUTH AFRICA

In the inland (plateau) regions of the Union of South Africa the seasonal change in weather conditions is fairly regular, with the bulk of the rain falling in thunderstorms during the summer months. Consequently, road temperature variations are also very regular except during the relatively short periods of continuous rain and on those days when rainstorms occur.

This regularity in road temperature change should enable the road engineer to choose a suitable grade of binder for successful resealing at any time of the year, his choice being based on a suitable measurement of the road surface temperature.

Road surface temperature data were collected at intervals over the period 1953–56 at two sites near Pretoria, and analysis of these data showed that the daily variation is remarkably regular except during rainy weather. Fig 2 shows the typical variation which takes place on a cold and on a hot day at an unshaded site. The minimum temperature occurs at sunrise and the maximum at about 1–2 p.m. In winter the minimum temperature might be as low as −2° C (28° F) at these sites, and in summer the maximum can be over 60° C (140° F). Not only is the pattern of change regular, but the difference between the maximum and minimum temperature is also fairly constant.

Fig 3 shows the distribution of the difference between the daily maximum and minimum road surface temperature during a period of one year for one of the sites (a similar distribution was obtained for the other site for a different 12-month period). The most fre-

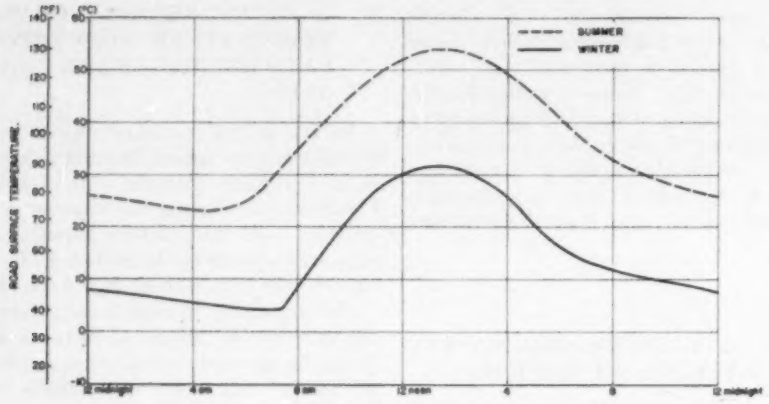

FIG 2

TYPICAL DAILY VARIATION OF ROAD SURFACE TEMPERATURE (MEASURED $\frac{1}{8}$ INCH BELOW THE SURFACE, UNSHADED SITE)

quently occurring values are about 29° C and 34° C (maxima on the curve). Examination of the data for the winter months April–July identified the 29° C value with this period and the 34° C value with the summer.

Under settled weather conditions, therefore, the road temperature conditions during any 24-hour period can be reasonably accurately predicted in the vicinity of Pretoria by measurement of the minimum (sunrise) or the maximum (midday) road temperature.

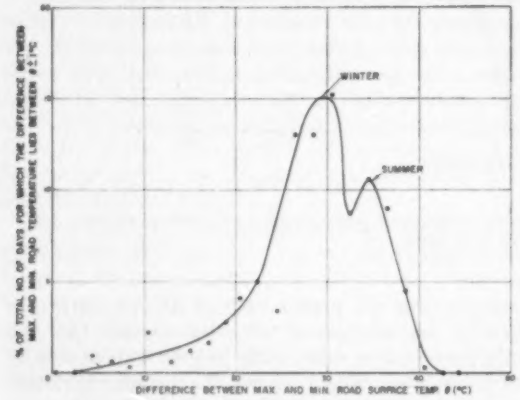
% OF TOTAL NO. OF DAYS FOR WHICH THE DIFFERENCE BETWEEN MAX. AND MIN. ROAD TEMPERATURE LIES BETWEEN θ ± 1°C
WINTER
SUMMER
DIFFERENCE BETWEEN MAX. AND MIN. ROAD SURFACE TEMP. θ (°C)

FIG 3

DISTRIBUTION OF THE DIFFERENCE BETWEEN DAILY MAXIMUM AND MINIMUM ROAD SURFACE TEMPERATURE DURING ONE YEAR FOR AN UNSHADED SITE (DATA FOR 311 DAYS)

C. SMALL-SCALE SINGLE-SEAL ROAD EXPERIMENT INVESTIGATING THE RELATIONSHIP BETWEEN ROAD SURFACE TEMPERATURE CONDITIONS AND STONE RETENTION BY DIFFERENT GRADES OF BINDER

In the period Feb–Sept 1959 a small-scale single-seal road experiment was laid on a lightly trafficked road near Pretoria carrying about 1200 vehicles/day. Single surface dressings were laid by hand both at sunrise (minimum) road surface temperature and at midday with a range of grades and types of binder and two different types of $\frac{1}{2}$–$\frac{3}{8}$-inch stone. The old road surface was a dense premix in good condition with a close even texture.

Traffic was allowed on to the sections soon after completion, and retention (coverage) of stone was assessed by a panel of five observers at least 48 hours after laying. By laying the same binder–stone combination at different times of the year, some information was obtained on the relationship between road temperature conditions and stone retention by the different grades and types of binder.

The lowest road temperatures at which complete coverage (retention) of stone was observed with the different binders are given in Table I. Since no significant difference was observed between the behaviour of the dolomite and quartzite aggregates used in the work, the different binder–stone combinations are not mentioned in the table.

The results given in Table I show that, by using low viscosity "cutback" binders, successful single resealing can be done at low temperatures. Under the conditions of the experiment there is only a slight advantage in laying the dressing at midday instead of at sunrise. Rapid wetting of the stone by the binder will take place at the maximum road temperature (see Section D (2)), but this is not a sufficient condition for ensuring permanent stone retention. Under the fast light traffic conditions of the experimental site the arrangement of the stones to form an interlocking mosaic is comparatively slow and, if the road temperature in the 24 hours subsequent to laying drops to a low value, "whip off" can take place because this mosaic has not been completely formed.

Formation of the stone mosaic is, of course, acceler-

ated by reducing the speed of the traffic over new work to a low figure or by repeated pneumatic-tyred rolling. Unfortunately, when resealing roads in rural areas of the Union of South Africa these conditions

TABLE I

Lowest Road Surface Temperatures Observed for Complete Coverage (retention) of Stone by the Different Grades and Types of Binder

(Rate of binder application in all cases was 0·20 gal/sq yd)

Type and grade of binder	Road surface temperature, ° C		
	Laying at sunrise	Laying at midday	
	Temp at time of laying	Temp at time of laying	Temp at subsequent sunrise
Persian petroleum bitumens (Agha Jari crude):			
M.C.4 * (197 sec Saybolt Furol viscosity at 82° C)	2·0 †	35·5 †	5·5 †
M.C.5 * (445 sec Saybolt Furol viscosity at 82° C)	9·0	31·5 ‡	2·5 (c)
Straight-run 190 pen bitumen . . .	16·0	45·0	12·0
Trinidad petroleum bitumens:			
M.C.4 * (262 sec Saybolt Furol viscosity at 82° C)	3·0 †	34·5 †	5·5 † (c)
M.C.5 * (576 sec Saybolt Furol viscosity at 82° C)	3·0 ‡	34·5	5·5 (c)
Straight-run 198 pen bitumen . . .	16·0	45·0	12·0
Coke-oven tars:			
30 EVT . . .	7·0 †	36·5 †	7·5 † (c)
38 EVT . . .	7·0	36·5	7·5 (c)
48 EVT . . .	12·0	38·5	10·5

(c) Calculated assuming that the difference between max and min road surface temperature was 29° C.

* Manufactured by cutting back 100 pen straight-run bitumen with kerosine.

† Lower temperatures not tested in the experiment.

‡ 95% stone coverage.

are seldom obtained, and the fast light traffic allowed on to new work tends to cause " whip off " before the stone mosaic can be formed.

It should be mentioned that the conditions of the small-scale experimental work differed in two respects from normal practice. The stone used was relatively free from dust (dust content, passing No. 36 mesh BS sieve—wet sieving, was 0·15 per cent by wt for the quartzite and 0·30 per cent by wt for the dolomite) and the time elapsing between the application of the stone and the binder was between one and two minutes. Both these conditions favour more rapid wetting of the stone than in some sealing practice. In the experimental work the sections were rolled with two passes of a light van and opened to traffic between 5 and 30 minutes after laying.

Information was also obtained from the road experiment on the relationship between binder viscosity at the road temperature and stone retention. The viscosities of the binders used in the experiment were measured at a series of temperatures in a conicylindrical viscometer [4] and the viscosity at the road surface temperature determined by interpolation of the data obtained. The relationship between the (bulk) viscosity of the binder at the minimum (sunrise) road temperature and stone retention for the different types and grades of binder is given in Table II.

TABLE II

Critical Viscosity Range (Measured at the Minimum Road Temperature) for the Transition from Complete to Incomplete Coverage of Stone (log poises)

Binder	Grade	Bulk viscosity, log poises			
		Laying at sunrise		Laying at midday	
		Complete coverage	Incomplete coverage	Complete coverage	Incomplete coverage
Trinidad petroleum bitumen	M.C. 4, M.C. 5 (winter)	4·9	5·8	5·3	6·4
	180/200 pen (summer)	6·3	6·7	6·7	6·9
Persian petroleum bitumen	M.C. 4, M.C. 5 (winter)	4·6	4·8	4·3	5·5
	180/200 pen (summer)	6·6	7·1	7·1	7·3
Coke-oven tar	25/30 and 35/40 EVT (winter)	4·5	5·5	5·3	6·4
	45/50 EVT (summer)	5·8	?	6·0	6·7

Under the conditions of the small-scale road experiment the less volatile binders (180/200 pen bitumens and 45/50 EVT tar) retain the stone at a higher (bulk) viscosity than the more volatile binders (cutback bitumens and low EVT tars). This difference is due, at least in part, to volatile oils evaporating from the surface of the cutback binder film at a faster rate than they are replaced by diffusion from the interior. This leads to a deficiency of volatiles on the surface of the film and, because the surface viscosity is higher than the bulk viscosity, wetting of the stone is slower (see Section D (3)). The critical viscosity for the retention of stone by the 180/200 pen grade straight-run bitumens is about 10^7 poises.

The road experiment did not reveal any significant difference in the behaviour of the two petroleum bitumens tested (Trinidad and Persian).

D. LABORATORY INVESTIGATIONS ON THE RATE OF WETTING OF " AIR-DRY " ROADSTONE BY BITUMENS

Adhesion of a bituminous binder to roadstone depends on many factors, but, allowing suitable conditions for the attainment of adhesion (wetting), the bond between the two materials must depend on their chemical properties at the interface. In most cases the " interface " properties are not the same as the properties of the materials in bulk. For example, constituents of the bitumen which are either polar

(*e.g.* acids and bases) or polarizable (*e.g.* aromatics) are likely to be concentrated at the interface. Similarly, the characteristics of a stone surface need bear no relation to the bulk characteristics of the crystalline mineral constituents of the stone. The ionic equilibrium present in the interior of a crystalline material can be profoundly changed at the surface of the crystal by rearrangement of position and effective charge of the ions to obtain a condition of minimum energy.[5] Furthermore, polar compounds present in the atmosphere and particularly water vapour will be absorbed on the surface.

Since the mineral surfaces present in roadstone are almost invariably hydrophilic, adhesion of the stone to a bituminous binder cannot normally be attained in the presence of liquid water (as opposed to water vapour). Air-dry roadstone, although in most cases having absorbed water on the surface, can, however, be wetted by bituminous binders to produce an adhesive bond. A dust layer is always present on the surface of such stone, and until this is wetted by the binder permanent adhesion cannot be obtained.

In the surface sealing operation one important factor in obtaining good stone retention is the speed with which adhesion is attained, *i.e.* the rate at which the binder wets the stone. This will depend not only on the forces of adhesion between the two materials but also on the resistance to flow of the binder surface. The viscosity of the binder at the surface would therefore be expected to play a very important part in the rate of wetting.

Some work has been done on the measurement of the rate of wetting of air-dry roadstone by bitumens and also on the physical and chemical properties of the bitumens and the stone which affect this process.

(1) *Development of a Method for Measuring the Rate of Wetting*

A simple test has been developed to measure the rate of wetting of an air-dry roadstone by a bituminous binder and was designed to imitate as closely as possible the conditions of wetting obtaining when a surface dressing is laid. It consists essentially of bringing a multi-layer of roadstone into contact with a film of binder under controlled conditions of temperature and humidity. Contact is maintained for a given time, and then the binder film is vibrated to remove all stone which is not adhering. The amount of stone remaining on the film is then determined by weighing.

It must be emphasized that this test is only intended to indicate the initial wetting condition in a surface-sealing operation and not the complicated action of pneumatic-tyred traffic in arranging the stone layer to form an interlocking mosaic.

The stone used for the test was a sieved fraction from which exceptionally elongated and flaky particles were removed by hand. Excess dust was removed by a simple water-washing procedure which left less than 0·1 per cent by wt of fine mineral matter (passing the 36-mesh sieve) adhering to the particle surfaces. The stone was placed in the apparatus at least 16 hours before being used in order to attain temperature and moisture equilibirum.

Test conditions affecting the amount of stone retained by the binder film were investigated as follows:

(a) *Humidity of Atmosphere in Apparatus*

The effect of varying the humidity from the dry condition (silica gel absorbent present) to 82 per cent humidity at 12°–16° C was investigated and, over the range studied, this factor had no effect on the amount of stone retained by the film.

(b) *Pressure on Stone Layer*

Applying pressure during the period of contact of the stone layer with the bitumen slightly increased the amount of stone retained.

(c) *Stone Size*

Three sizes of stone were tested and repeatability of test results was found to improve as the stone size was decreased. To avoid departing too much from the condition of the road surface dressing operation it was decided to use $\frac{5}{16}$–$\frac{1}{4}$-inch size stone for the standardized test procedure.

(d) *Method of Preparation of the Binder Film*

The binder was spread on to the test tray with a minimum of heat treatment. Exposure of the film to ultra-violet light for a short time was found to reduce the amount of stone retained, and the films were therefore kept out of contact with direct sunlight during preparation. A description of the standardized test procedure is given in Appendix A.

(2) *Comparison of the Behaviour of the Different Types of Straight-Run Bitumen in the Rate of Wetting Test*

It has already been mentioned that the rate of wetting of a stone by a bitumen will depend not only on the forces of adhesion between the two materials but also on the surface viscosity of the binder film.

This can be demonstrated by exposing a film of bitumen for 5 minutes at room temperature to an ultra-violet lamp and then testing for rate of wetting. The increase in surface viscosity of the film caused by photo-oxidation produces a significant reduction in stone retention. Such an effect may be of some importance on the road, as undue delay between spraying a binder and application of the stone may give rise to appreciable surface oxidation of the binder by the action of sunlight.

Although, in general, it cannot be assumed that surface viscosity is the same as bulk viscosity, this may be approximately true for straight-run bitumens

of low volatility and low susceptibility to oxidation. On this assumption, the rate of wetting of different 150/200 pen grade straight-run bitumens has been compared on the basis of bulk viscosity at the test temperature. Standard test results on the bitumens

A comparison of the wetting test results obtained with the Venezuelan, the Saudi Arabian, and the Persian (Agha Jari) bitumen is shown in Fig 4, in which the amount of stone retained by the film is plotted against bulk viscosity of the bitumen at the

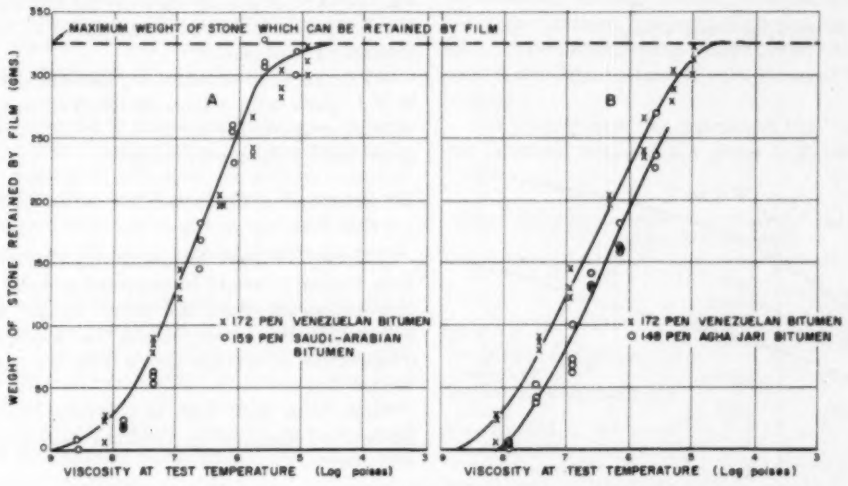
MAXIMUM WEIGHT OF STONE WHICH CAN BE RETAINED BY FILM
WEIGHT OF STONE RETAINED BY FILM (GMS)
A
B
x 172 PEN VENEZUELAN BITUMEN
o 159 PEN SAUDI-ARABIAN BITUMEN
x 172 PEN VENEZUELAN BITUMEN
o 148 PEN AGHA JARI BITUMEN
VISCOSITY AT TEST TEMPERATURE (Log poises)
VISCOSITY AT TEST TEMPERATURE (Log poises)

FIG 4

THE EFFECT OF TEMPERATURE ("BULK" VISCOSITY) ON STONE RETENTION BY DIFFERENT TYPES OF BITUMEN

are given in Table III, and results of other physical and chemical tests are given in Table IV. Although the standard test results do not reveal any important differences between the six bitumens, the other tests showed that the Persian and Saudi Arabian bitumens contained more wax than the Trinidad and Venezuelan

TABLE III

Standard Test Results (IP Methods) on Four Petroleum Bitumens from Different Crude Sources

Bitumen	Western Hemisphere		Middle East	
	1	2	3	4
Crude source	Venezuelan	Trinidad	Saudi Arabia	Persia (Agha Jari)
Penetration at 25° C	172	186	164	149
Specific gravity, 15/15° C	1·017	1·006	1·017	1·015
Softening point (R and B), °C	40·0	38·2	40·9	39·6
Loss on heating test:				
Loss in weight, %	0·3	0·2	0·2	0·2
Penetration of residue as a % of the original	90	93	86	65
Bitumen content (soluble in CS_2), % wt	99·3	100	99·9	100

bitumens and less acidic material. The susceptibilities of the bitumens to oxygen attack (as measured by the pressure oxidation test) were all low and of the same magnitude, but the Persian bitumen had a significantly higher temperature susceptibility of viscosity than the Trinidad and Venezuelan bitumens.

test temperature. In these tests a reef quartzite stone was used, and the time of contact between the stone and the bitumen film was 5 minutes.

TABLE IV

Results of Various Physical and Chemical Tests on Four Petroleum Bitumens from Different Crude Sources

Bitumen	Western Hemisphere		Middle East	
	1	2	3	4
Crude source	Venezuelan	Trinidad	Saudi Arabia	Persia (Agha Jari)
Viscosity/temp characteristics:				
EVT, °C	68·6	65·0	65·8	64·9
Viscosity at 25° C, poises	$2·0 \times 10^8$	$1·7 \times 10^8$	$2·0 \times 10^8$	$3·8 \times 10^8$
Temperature coefficient of viscosity *	9·2	9·6	10·2	11·3
Temperature susceptibility index †	11·2	12·0	12·5	13·2
Increase in EVT on pressure oxidation, °C (72 hr at 65° C—20 atmospheres oxygen—bitumen film 7 mm thick)	7·1	7·8	8·2	6·8
Wax content, % wt (chromatographic method) ‡	0·2	0·4	5·0	5·0
Acid value ml $\frac{N}{10}$ per g (by potentiometric titration in methanol/benzene solvent) §	0·49	0·43	0·02	<0·01

* This coefficient is defined as the rate of change of viscosity (measured in log poises) with temperature (measured in log °F units). It is approximately constant over the temperature range 10°–50° C.

† This index is substantially independent of viscosity and is defined by the expression $\frac{(\text{Temperature coefficient of viscosity} + 3)}{(40 + \text{EVT, °C})} \times 100$.

‡ The chromatographic method used for the determination of wax content is described in Appendix B.

The data given in Fig 4 show the important effect of binder viscosity on the rate of wetting, but indicate only small differences between the different types of bitumen. The Persian (Agha Jari) bitumen appears

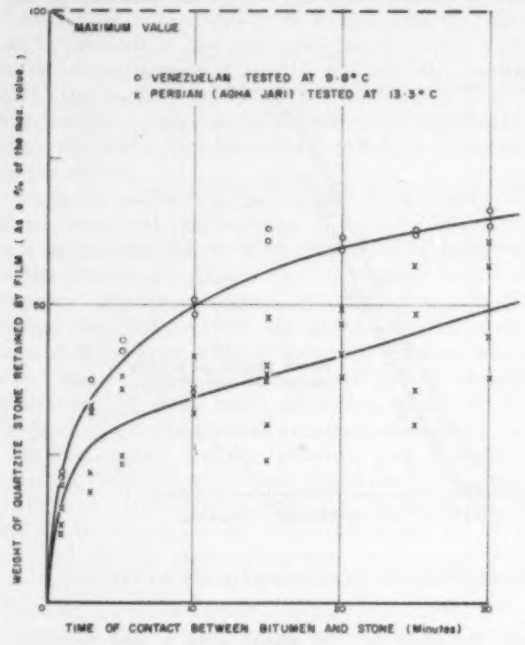
MAXIMUM VALUE
o VENEZUELAN TESTED AT 9·8° C
x PERSIAN (AGHA JARI) TESTED AT 13·3° C
WEIGHT OF QUARTZITE STONE RETAINED BY FILM (As a % of the max. value)
TIME OF CONTACT BETWEEN BITUMEN AND STONE (Minutes)

FIG 5

THE RATE OF WETTING OF A VENEZUELAN AND A PERSIAN BITUMEN (150–200 PEN GRADE) AT A BULK VISCOSITY OF 10^7 POISES

to have slightly poorer wetting properties than either the Venezuelan or the Saudi Arabian bitumens.

A more detailed comparison of the wetting behaviour of the Persian and Venezuelan bitumens is shown in Fig 5, where the amount of reef quartzite stone retained by the bitumen film (expressed as a percentage of the maximum which can be retained) is plotted against time of contact between the stone and bitumen. The bitumens were tested at temperatures such that their bulk viscosity was 10^7 poises.

Although the scatter of results was much greater with the Persian bitumen than with the Venezuelan bitumen, the rate of wetting of the quartzite stone is definitely faster with the latter. Even after 30 minutes of contact at this bulk viscosity, however, the Venezuelan bitumen attained only 65 per cent of the maximum possible stone retention. Efforts to improve the repeatability of the test when using Persian bitumen were unsuccessful, suggesting that, in this case, the surface of the film might be heterogeneous.

In order to eliminate any effect of temperature on wetting properties other than its effect on viscosity, it would be desirable to compare the behaviour of bitumens not only at the same bulk viscosity but also at the same temperature of test. A bitumen of Trinidad petroleum origin was prepared from a mixture of 100 pen and 200 pen straight-run grades such that its bulk viscosity was 10^7 poises at 13·3° C (the test temperature for the 200 pen Persian bitumen). The rate of wetting test result on this bitumen at 13·3° C was found to be not significantly different from that on the 200 pen Trinidad bitumen tested at 10·0° C (bulk viscosity 10^7 poises).

With this type of bitumen, therefore, over a range of 3° C there is no detectable effect of temperature on wetting properties other than that expected from that produced by change in viscosity.

(3) *Behaviour of Cutback Bitumens in the Rate of Wetting Test*

Although cutback bitumens, by virtue of their low bulk viscosity, would be expected to have better wetting properties than the more viscous straight-run bitumens, this effect might be modified by the evaporation of volatile fluxes from the surface of the binder film.

Tests have been done to compare the wetting behaviour of straight-run Trinidad petroleum bitumens

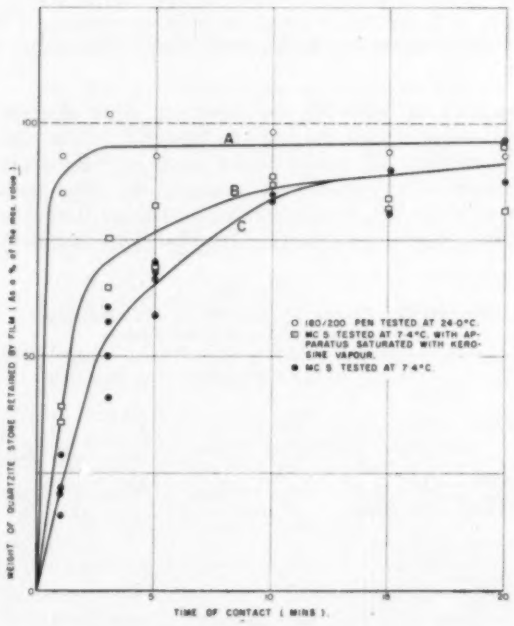
A
B
C
o 180/200 PEN TESTED AT 24·0°C.
□ M.C.5 TESTED AT 7·4°C. WITH APPARATUS SATURATED WITH KEROSINE VAPOUR.
● M.C.5 TESTED AT 7·4°C.
WEIGHT OF QUARTZITE STONE RETAINED BY FILM (As a % of the max. value)
TIME OF CONTACT (MINS).

FIG 6

RATE OF WETTING TEST RESULTS ON CUTBACK AND STRAIGHT-RUN TRINIDAD PETROLEUM BITUMENS TESTED AT A BULK VISCOSITY OF 2×10^5 POISES

and M.C.5 grade bitumens made up from 100 pen Trinidad bitumen and either kerosine or coal tar naphtha.

A 200 pen grade bitumen and the M.C.5 grade

material were tested at the same bulk viscosity (2×10^5 poises), the binder film being left in the apparatus for 3 hours before applying the reef quartzite stone. The results of these tests are given in Fig 6 (curves A and C).

For contact times of up to 10 minutes the rate of wetting of the 200 pen bitumen is very much faster than that of the M.C.5 grade material tested at the same bulk viscosity. For longer times of contact both bitumens approach the maximum stone retention value.

Some improvement in the initial wetting of the cutback bitumen was obtained by saturating the atmosphere in the apparatus with kerosine vapour (curve B, Fig 6). Even under these conditions, however, the rate of wetting was not so rapid as with the 200 pen grade material at the same bulk viscosity (curve A, Fig 6).

The same series of tests was done on an M.C.5 grade bitumen made from the 100 pen grade Trinidad petroleum bitumen base and a coal tar naphtha flux with similar volatility characteristics to the kerosine used in the first series of tests. The results obtained were very similar to those in which kerosine was used, and the effect of flux vapour in increasing the initial rate of wetting was confirmed.

The wetting behaviour of the cutback bitumens can, therefore, be explained by rapid evaporation of volatile flux from the surface of the film and comparatively slow replacement of this loss by diffusion from the interior. This temporarily produces a higher viscosity at the surface than in the interior of the film, and rate of wetting is reduced.

(4) *Effect of Removal of Wax from the Persian Bitumen on its Wetting Properties*

The Persian (Agha Jari) bitumen contains a high proportion of waxy constituents (see Table IV), and these partially crystallize from the bitumen at ambient temperature to give its surface a dull appearance. Leaching tests on films of the bitumen showed, however, that wax crystallization takes place throughout the bitumen, and there is no significant concentration of wax crystals at the air/bitumen surface.

To determine if the wax affects the wetting properties of the bitumen for stone, a 180/200 pen grade straight-run Agha Jari bitumen was partially dewaxed and its rate of wetting on quartzite stone was measured. Dewaxing was effected by chromatographing a pentane solution of the bitumen over alumina and isolating a paraffin-rich fraction. The wax in this fraction was separated by crystallization from ethanol (96 per cent)/ether solvent at $-25°$ C and the dewaxed eluate was then combined with the material insoluble in pentane and that remaining absorbed on the column. (The material absorbed on the column was removed by pyridine elution followed by carbon disulphide elution.) By this process, 8·9 per cent of soft wax (mp 108° F) was removed from the bitumen and the operational losses were 3·2 per cent by wt. The surface of the recovered bitumen was shiny and appeared to be free from wax crystals. To eliminate the possibility that the chromatographic procedure itself might affect the wetting properties of the bitumen, another bitumen was prepared by exactly the same process but excluding the wax separation step. The wetting properties of this " control " bitumen were then compared with those of the dewaxed material.

The properties of the untreated, the " control," and the dewaxed bitumen are given in Table V.

TABLE V

Properties of the Dewaxed, the " Control," and the Untreated Agha Jari Bitumen

	Untreated	" Control "	Dewaxed
EVT, ° C	64·1	68·2	78·3
Temperature coefficient of viscosity	10·9	12·0	12·9
Temperature susceptibility index	13·4	13·8	13·4
Wax content, % wt (chromatographic method). See Appendix B	5·0	4·9	2·7
Temperature at which the viscosity is 7·0 log poises, ° C	13·3	16·0	23·2

Partial dewaxing of the bitumen, although increasing its viscosity, did not alter its temperature/viscosity characteristics. Despite the fact that 8·9 per cent by wt of wax had been removed, the decrease in wax content, according to the analytical method used, was only 2·2 per cent by wt. Although the analytical method may be a useful indication of differences in chemical composition between the different types of bitumen, it obviously provides only an arbitrary measure of the waxy constituents. Subjecting the bitumen to the chromatographic separation process (" control " bitumen) slightly increased its viscosity.

Rate of wetting test results for the untreated bitumen (curve A), the " control " bitumen (curve B), and the dewaxed bitumen (curve C) are given in Fig 7, all the bitumens being tested at a bulk viscosity of 10^7 poises. The chromatographic separation process (" control ") slightly improved the wetting properties of the bitumen, but the wetting properties of the dewaxed bitumen are not significantly different from those of the untreated material. These results suggest that the waxy constituents do not play an important role in the wetting behaviour of the Persian bitumen on " air-dry " quartzite stone.

(5) *The Effect of Dust on the Surface of the Stone on Wetting Properties*

All roadstones have a layer of dust tenaciously adhering to the surface, and the amount is conveni-

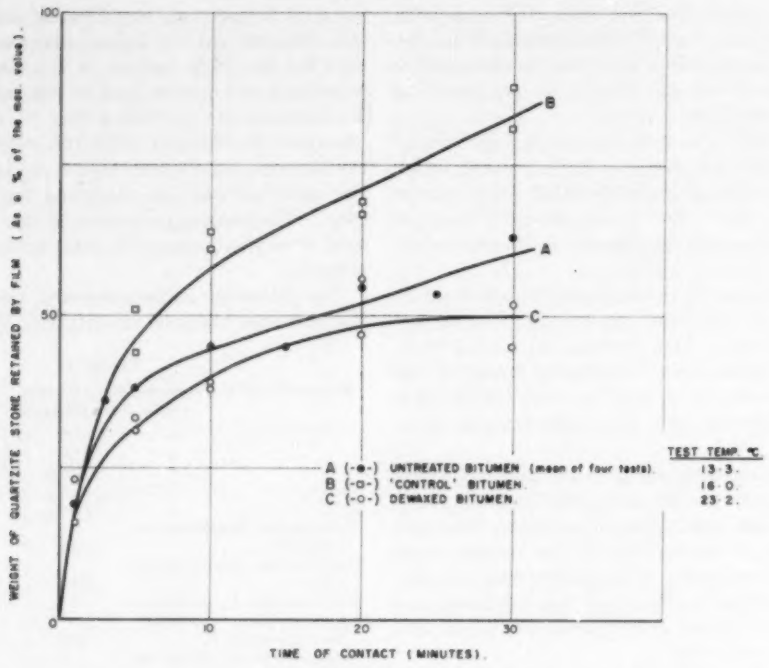

FIG 7

THE EFFECT OF PARTIAL DEWAXING ON THE RATE OF WETTING OF A QUARTZITE STONE BY A PERSIAN BITUMEN/TESTS AT A BULK VISCOSITY OF 10^7 POISES

ently measured by washing the stone with a 0·5 per cent wt solution of sodium oxalate in distilled water through a No. 36 BS mesh sieve. The dust suspended in the sodium oxalate solution is then separated by filtration, washed with distilled water, and weighed.

The effect of the amount of dust on the surface of the reef quartzite on the rate of wetting by a Trinidad petroleum bitumen is shown in Fig 8.

With unwashed stone having a dust content of 0·1 per cent wt, wetting is slow compared with the washed stones. The removal of the last traces of dust by washing with an 0·5 per cent solution of sodium oxalate in water did not, however, significantly change the rate of wetting from that obtained with stone washed with tap water.

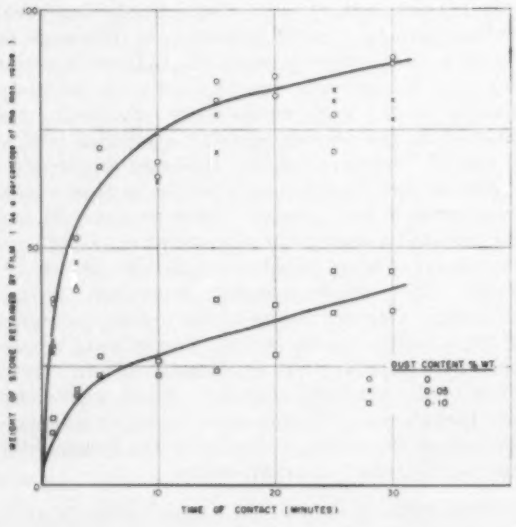

FIG 8

THE EFFECT OF DUST ON THE RATE OF WETTING OF A QUARTZITE BY A 200 PEN GRADE TRINIDAD PETROLEUM BITUMEN/TESTS AT 10° C AND A BULK VISCOSITY OF 10^7 POISES

(6) *The Effect of Stone Type on Rate of Wetting*

Preliminary tests comparing the rate of wetting of washed reef quartzite and dolomite by both the Persian and the Venezuelan bitumens suggested that stone type would have little or no effect on this property.

This was not generally confirmed by measurements of the rate of wetting of the Trinidad petroleum bitumen on samples of seven different washed stones in the "air-dry" condition.

The common names, geological description, and dust content of these stones is given in Table VI. The results of rate of wetting tests with these stones, using Trinidad petroleum bitumen at a bulk viscosity of 10^7 poises, are given in Fig 9.

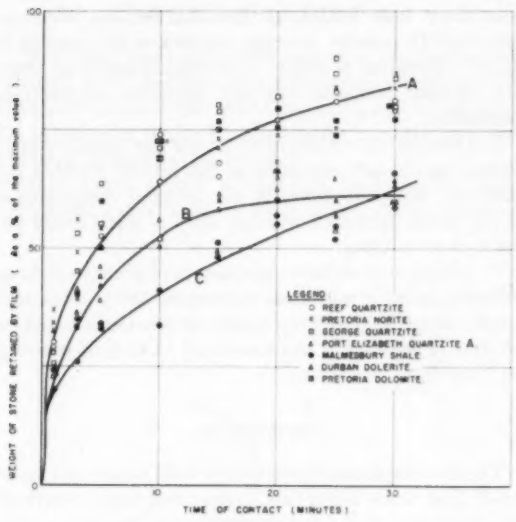

FIG 9

THE RATE OF WETTING OF A 200 PEN GRADE TRINIDAD PETROLEUM BITUMEN OF SEVEN DIFFERENT TYPES OF "WASHED" STONE/TESTED AT 10° C AND A BULK VISCOSITY OF 10^7 POISES

TABLE VI

The Common Name, Geological Description, and Dust Content of the Seven Stones Tested

Common name	Geological description	Dust content, % wt
Reef quartzite	A hard recrystallized quartzite from the Witwatersrand series	0·05
Pretoria dolomite	A fine-grained sedimentary rock essentially carbonates of calcium and magnesium from the dolomite series of the Transvaal system. Slightly weathered	0·06
Pretoria norite	A coarse-grained basic igneous rock consisting essentially of Plagioclase felspar and Pyroxene. From the bush-veld complex	0·06
Durban dolerite	A fine-grained intermediate igneous rock consisting essentially of Plagioclase felspars. Porphyritic. Post-Karroo system age	0·04
Port Elizabeth quartzite A	A fine-grained hard recrystallized quartzite from the Table Mountain sandstone of the Cape system. Slightly weathered	0·03
George quartzite	A very hard recrystallized quartzite probably from the Congo formation	0·04
Malmesbury shale	A hard, indurated, blue rock of sedimentary origin	0·04

The Reef quartzite, Pretoria norite, George quartzite, and the Pretoria dolomite all show similar wetting properties (curve A), while the Port Elizabeth quartzite and the Durban dolerite have definitely inferior wetting properties, particularly at the longer times of contact (curve B). The Malmesbury shale (curve C) shows comparatively poor wetting properties at the shorter times of contact.

These results show that the type of stone may have some effect on rate of wetting. Although the stones had roughly the same dust content, it is possible that the nature of this dust may have some effect on rate of wetting, and further work is needed to clarify this point.

E. THE EFFECT OF ADDITIVES ON THE INITIAL ADHESION OF BITUMENS TO "AIR-DRY" ROADSTONE

The effect of various types of additive on the initial adhesion of bitumen to the reef quartzite was tested in the laboratory by means of the rate of wetting test. All the tests were done with 180/200 pen grade bitumens at a bulk viscosity of 10^7 poises, and stone retention was measured after 5, 15, and 30 minutes contact time. For small concentrations of additive (up to 1 per cent wt) no adjustment was made in the test temperature for the small change in viscosity produced by the additive.

Three broadly different groups of additives were examined: long-chain polymers, including natural and synthetic rubbers; bitumen soluble materials containing fatty acids and esters; and cationic wetting agents.

The results of the tests were as follows:

(1) *Long-Chain Polymers*

Addition of an oil soluble methacrylate polymer or polyvinyl acetate (added to the bitumen as latex) at concentrations up to 0·5 per cent by wt produced a small increase in the rate of wetting of quartzite by the Persian bitumen. Natural rubber and butadiene–styrene copolymer (GRS), both added as latexes, gave only a slight increase in the rate of wetting at short contact times, and an epoxy resin gave no significant improvement in rate of wetting at a concentration of 0·5 per cent by wt.

(2) *Bitumen Soluble Materials Containing Fatty Acids and Esters*

Stearic acid (1 per cent by wt), refined lake asphalt from Trinidad (20 per cent by wt), olive oil (0·5 to 2·0 per cent by wt), and natural resin (0·5 per cent by wt) were tested. None of these additives produced a significant change in the rate of wetting of the quartzite stone by the Persian bitumen.

(3) *Cationic Wetting Agents*

Two proprietary cationic wetting agents, one a long-chain diamine, were tested at a concentration of 1 and 2 per cent wt. Neither additive produced a significant

change in the rate of wetting of the quartzite stone by the Persian bitumen.

Except possibly by adding certain long-chain polymers, the laboratory tests did not indicate any promise of improvement in the rate of wetting of quartzite by the Persian bitumen. Road sections were laid, however, to determine if there was any improvement of stone retention in the single resealing operation by using such additives. Test strips, using the small-scale technique described in Section A, were laid with bitumens containing additives, and "control" strips, using the untreated bitumen, were laid under the same road temperature conditions.

The additives used in the road tests were the oil soluble methacrylate polymer, polyvinyl acetate, natural rubber, GRS synthetic rubber, olive oil, and one of the proprietary cationic wetting agents. None of these produced any significant improvement in retention of stone by the bitumens when the dressings were laid at sunrise (minimum road temperature). In one series of test strips the addition of 2 per cent of natural rubber gave a slight improvement in stone retention when the dressing was laid at midday (maximum road temperature).

CONCLUSIONS

1. Small-scale road experiments have indicated that, when resealing fast, lightly-trafficked roads under dry weather conditions, complete stone retention depends on the road surface temperature at the time of laying and during the subsequent 24 hours.

2. Under the settled weather conditions often prevailing in the inland regions of the Union, the road surface temperature at sunrise can be used as a guide to road temperature conditions during the subsequent 24 hours.

3. The small-scale road experiment gave an indication of the lowest sunrise road temperatures at which the different viscosity grades of binder would hold a complete cover of chippings when resealing under the conditions described.

4. Laboratory tests on the rate of wetting of "air-dry" roadstone by bitumens have indicated that the most important factor affecting the speed of the wetting process is the surface viscosity of the bitumen film.

5. Cutback bitumens, although suitable for resealing under cold conditions, are not so effective as would be expected from their low bulk viscosity. Rapid evaporation of "cutting-back" oil from the surface of the bitumen film produces an increase in viscosity at the surface and a reduction in the initial rate of wetting.

6. Although, in the small-scale single resealing road experiment, no significant difference was observed between the stone retention behaviour of bitumens derived from Persian and Trinidad crude petroleums, laboratory tests indicated that the Persian bitumen had slightly inferior wetting properties for quartzite stone. Removal of about 9 per cent of soft wax from the Persian bitumen did not improve its wetting properties.

7. Dust on the surface of the stone was found to produce a significant reduction in the rate of wetting by bitumen, but differences in the mineral composition of the stone appeared to have only a small effect on the rate of wetting.

8. Addition of either long-chain polymers (including rubbers), soluble materials containing fatty acids and esters, or cationic wetting agents to bitumens failed to produce a significant improvement in rate of wetting on "air-dry" roadstone.

DISCUSSION

The investigation described in this paper has indicated that when using the "spray and chip" method for resealing fast, lightly-trafficked roads in dry weather two conditions must be fulfilled for successful retention of stone.

> (*a*) The binder film must have a sufficiently low surface viscosity at the prevailing road surface temperature to ensure rapid wetting of the stone.
>
> (*b*) The binder film must have a sufficiently low bulk viscosity during the first 24 hours after application so that the stone can move reasonably freely under the action of pneumatic-tyred traffic and form an interlocking mosaic in which individual stones have lateral support from their neighbours.

The use of dusty stone or a grade of binder whose viscosity is too high for the prevailing road temperature conditions will give slow wetting of the stone. Also, the use of stone with a wide range of sizes or a binder whose viscosity is too high during the period following laying will reduce the rate of formation of the stone mosaic. With a stone of wide grading the larger sizes tend to stand proud of the surface and are preferentially "whipped off" by fast traffic.

Even if good initial wetting is obtained when the stone is in the "air-dry" condition, it is possible that wet weather following the laying could, in certain circumstances, affect the performance of the seal. Wilhelmi and Schultze [7] and, more recently, Hughes, Lamb, and Pordes [8] have found that water diffuses slowly through the binder film to the stone surface to form a "detached" state.

The strength of the binder–stone bond in this detached state may be comparatively low in shear and, unless good lateral support of the stone has been achieved by mosaic formation, "whip off" under traffic may take place if the wet condition is sufficiently prolonged.

ACKNOWLEDGMENTS

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APPENDIX A

Standardized Test Procedure for the Measurement of the Rate of Wetting of "Air-Dry" Roadstone by Binders

(1) *Apparatus*

A diagram of the apparatus is shown in Fig 10. It consists of a constant temperature and humidity cabinet in which six binder films can be tested. The vertical vibrating table used to remove stone not adhering to the binder film is also shown in the figure. The temperature of the cabinet is controlled to within $\pm 0{\cdot}2°$ C of the desired value and the relative humidity is controlled to 50–55 per cent at 12°–16° C by placing a large dish containing a saturated solution of sodium dichromate in the cabinet. Tests are normally done in the temperature range 0° to +30° C.

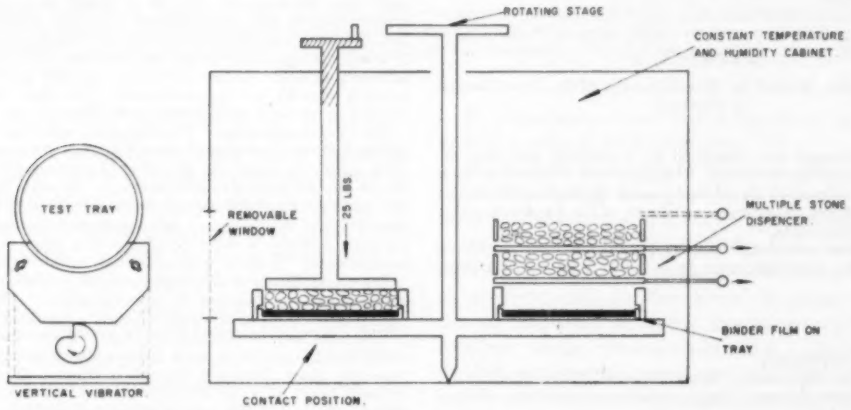


FIG 10

DIAGRAM OF RATE OF WETTING TEST APPARATUS

(2) *Preparation of Stone for the Test*

Commercially supplied roadstone is screened to isolate the fraction passing the $\frac{5}{8}$-inch mesh BS sieve and retained on the $\frac{1}{4}$-inch mesh BS sieve. Exceptionally elongated and flaky particles are removed from this fraction by hand and excess dust is then removed by washing in a slow stream of tap water.

The washed stone, after being dried in trays at ambient temperature, is placed in the six stone dispensers of the testing apparatus (at least 16 hours before testing begins). The dispensers are completely filled with stone.

(3) *Preparation of the Binder Film*

40 ml of binder are weighed on to the circular test tray ($40 \pm 0{\cdot}1$ g of a bitumen of sp gr 1·0), and this is placed in an oven at 110° C. As soon as the binder is fluid enough to spread, the tray is removed from the oven and tilted so that the binder completely covers the bottom. The tray is then placed on a horizontal surface to obtain an even film. Any air bubbles on the surface can be removed by "pricking" with a hot wire. After cooling to room temperature the trays are then placed in the holders of the rotating stage of the testing apparatus and kept at least 2 hours in the constant temperature cabinet before testing.

Care must be taken that the binder film is not exposed to direct sunlight during preparation. The thickness of the binder film on the trays is equivalent to a rate of binder application of 0·18 gal/sq yd.

(4) *Test Procedure*

A tray is charged with a multi-layer of stone by withdrawing the lowest stone dispenser shield rapidly. The charged tray is then moved to the pressure position by rotating the stage through 180°. Pressure (a weight of 25 lb) is then applied for the required time of contact. At the end of this time the charged tray is rapidly removed from the cabinet and fastened in the vertical vibrator. After shaking 20 times the tray, with any adhering stone, is weighed.

(5) *Evaluation*

The weight of stone retained by the binder film is expressed as a percentage of the maximum weight which can be retained with the particular stone being tested. The maximum weight

D

is determined by doing six tests at a sufficiently high temperature and a sufficiently long contact time to ensure maximum retention. The mean of the six results is taken as the maximum.

(6) *Repeatability*

The repeatability of the test depends to a certain extent on the type of binder being tested. With the Trinidad bitumen and quartzite stone, a coefficient of variation from the mean of from 7·5 to 9·5 per cent was obtained for different times of contact. With the Persian bitumen and quartzite stone the coefficient ranged from 10 to 27 per cent for different times of contact.

APPENDIX B

Chromatographic Method for Determination of the Wax Content of Bitumen

Outline

20 g of bitumen are dissolved in *n*-pentane and the insolubles removed by filtration. The solution obtained is then reduced to a volume of 50 ml and passed through a column of activated alumina to separate an eluate of the predominantly paraffinic constituents.

Crystallizable waxes are then isolated from this paraffinic concentrate by crystallization at $-20°$ C from ether/alcohol solution.

Materials

n-Pentane (technical).

Alumina 100–200 mesh. Type H grade (Peter Spence).

Crystallization solvent—equal volumes of absolute ethanol and di-ethyl ether.

Benzene—crystallizable grade.

Apparatus

The chromatography column consists of a 120-cm glass tube of internal diameter 2·2 cm with a ground glass tap at the base. A one-litre dropping funnel at the top of the column acts as solvent reservoir.

Procedure

(1) *Removal of Insolubles from Pentane Solution.* 20 g $\pm$ 0·05 g of bitumen are dispersed in 100 ml pentane at room temperature. The dispersion is then diluted with a further 200 ml of pentane and the precipitated material removed by filtration through a sintered glass Buchner funnel of porosity 2. The precipitate is washed with a further 100–120 ml pentane. The volume of the bitumen solution and washings is then reduced by distillation to 50 ml $\pm$ 2 ml.

(2) *Preparation of the Column.* 320 ml *n*-pentane are poured into the tube, previously plugged with glass wool, and a perforated plunger inserted. 400 g $\pm$ 2 g alumina (activated by placing overnight in an open flat tray in an oven at 150° C and then allowed to cool in a closed container) are then poured slowly into the column. As the alumina is poured into the tube the plunger is given an " up and down " motion to release trapped air from the particles and to compact the alumina evenly. When correctly packed the height of the column should be approximately 110 cm. Solvent must always be present above the top of the column.

(3) *Chromatography.* The bitumen solution is poured on to the column and a graduated receiver (or volumetric flask) with a narrow neck and shield is placed close under the exit of the tap to minimize evaporation. Elution is then carried out until the total volume of eluate is 500 ml $\pm$ 0·05 ml. The first 200 ml of eluate are discarded and the last 300 ml are vacuum-distilled to remove solvent and recover the paraffinic concentrate. This is weighed to the nearest mg.

(4) *Crystallization Procedure.* 0·75 $\pm$ 0·05 g of paraffinic concentrate are dissolved in 50 ml of diethyl ether (dried over $CaCl_2$) and 50 ml of absolute ethanol are added.

The solution is allowed to stand in an ice/salt bath at $-20°$ C for one hour and then rapidly filtered through a sintered glass Buchner funnel (porosity 3) cooled by an ice/salt bath at $-20°$ C. The filter is washed with three 20-ml portions of the mixed solvent cooled to $-20°$ C. The waxes on the filter are then dissolved in crystallizable benzene and the benzene removed from the solution contained in a wide-necked flask, first by distillation and then in a vacuum oven at 70° C until the flask is of constant weight.

(5) *Repeatability of Test.* The mean of nine tests on the Persian bitumen was 5·02 per cent by wt and the standard deviation from the mean was 0·29 (coefficient of variation 6 per cent).

STUDIES IN SHALE OIL. PART X. TAR BASES AND GUM FORMATION IN SHALE GASOLINE *

By GEO. E. MAPSTONE † (Fellow)

SUMMARY

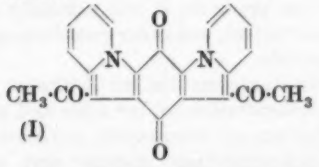
Pyridine homologues, quinones, and carboxylic acids or ketones readily condense in hydrocarbon solution to give resinous products possessing the appearance and characteristics of the gum deposited from raw shale gasoline and naphtha. It is suggested that similar reactions may be responsible for the rapid gum formation in these products.

INTRODUCTION

One of the characteristics of raw shale gasolines and naphthas is the very ready formation of gum. Dinneen and Bickel [1] have shown that the principal difference between these gums and the gums from petroleum naphthas is that the shale gums contain a high percentage of nitrogen (about 8 per cent). These workers showed that oxidation was much more important than light and heat in promoting the formation of gum, and that the nitrogen came from both the pyrrole and pyridine compounds in the oil. The work reported in this paper reconciles this observation with the apparently contradictory observation that the purified pyridine homologues have a slight inhibiting action when added to a refined shale gasoline.[2]

Bu'Lock and Harley-Mason showed [3] that quinones readily condensed with indoles in the presence of acid to give strongly coloured indolyl-quinones, a reaction which has been made the basis of tests for indoles or pyrroles [4] and for quinones.[5] This reaction, and the polymerization of pyrroles to " pyrrole red," explain the final deepening in the colour of raw shale pressure distillate after acid treatment; but they fail to explain the red colour obtained when quinones are added to gasoline containing pyridine homologues [6] and which turns yellow on acidification.

The reaction involved between the pyridine bases and quinone appears to be unknown. It was first considered possible that it may involve a side chain aldol-type condensation analogous to the condensation of α- and γ- alkyl pyridines with aldehydes and ketones, but there appears to be no mention of such a reaction in the literature. However, pyridine, quinone, and acetyl acetone are known to react vigorously to give an insoluble dark green compound [7,8] which has the structure:[9]



(I)

This reaction is but one example of the condensation of pyridines with diketones.[10-12]

While investigating the above reaction the author found that when acetyl acetone was replaced with acetone there was also a very vigorous reaction which gave an almost black product which was red-brown in thin layers. The product was virtually insoluble in gasoline, but in thin films on glass it appeared almost identical with the insoluble deposit left by oxidized shale pressure distillate. Since traces of methyl ethyl ketone have been detected in Australian [13] and South African [14] shale gasolines, and a wide range of ketones has been isolated from Estonian shale oil fractions,[15] much of the colour formation referred to above between the tar bases and quinone and for the discoloration of the pressure distillate on oxidation could possibly be due to the formation of compounds such as I. The condensation of some tar bases with ketones and quinones was therefore examined. Since there are usually some trace amounts of carboxylic acids also present in shale oils,[16-19] they were tested as carbonyl compounds along with the ketones.

EXPERIMENTAL

The addition of pyridine to a 10 per cent solution of quinone in acetone initiated a strongly exothermic reaction. The almost colourless solution rapidly turned dark brown and then black and gave a black gummy deposit which was readily soluble in excess pyridine but less so in acetone. This deposit was very similar in appearance, solubility, colour, and general characteristics to the resinous deposit from unrefined light shale distillates on standing.

Pyridine, quinoline, and redistilled, pyrrole-free shale tar bases (distilling to 220° C) were dissolved in *n*-heptane to give 0·4M solutions. Similar 0·4M solutions of acetone, methyl ethyl ketone, acetic and formic acids, and approximately saturated solutions of quinone (0·006M), α- and β-naphtha-quinones (0·009M), and anthraquinone (0·0026M) were prepared in *n*-heptane.

To a mixture of equal volumes of the base and

* MS received 23 May 1960. † Dermacult (S.A.) Pty Ltd, P.O. Box 726, Johannesburg, South Africa.

ketone of acid solutions was added sufficient of the quinone solution to give a final ratio of one mol of quinone to two mol of base and of the ketone or acid. Blank sets of solutions were also prepared in which *n*-heptane alone was added in place of either the ketone or acid of the quinone.

The final solutions (approximately 20 ml) were allowed to stand in loosely stoppered test tubes. After three weeks most solutions had deposited a resinous or gummy material on the sides or bottom of the test tube, but in no case was there a deposit in the absence of a quinone or in the presence of anthraquinone. Differences in the amount of deposit were slight, but the general trends of decreasing reactivities appeared to be in the order:

1. Bases: shale tar bases; quinoline; pyridine.
2. Carbonyl compounds: formic acid; acetic acid; acetone; methyl ketone; *nil*.
3. Quinones: β-naphtha quinone; α-naphtha-quinone; quinone.

The initial deposits were not removed from the solutions, which were allowed to evaporate to dryness from the loosely corked test tubes. During the evaporation the deposits progressively increased in amount, but in no case was there a visible change in appearance. When evaporation was complete, dark brown resins had been formed from all combinations of bases and quinones other than anthraquinone. The residues were all insoluble in boiling *n*-heptane but readily soluble in acetone. They all had the typical appearance of gum deposits from unrefined gasoline evaporated from test tubes in the same way. All deposits showed high nitrogen contents by the Lessaigne reaction.

DISCUSSION

The results obtained show that the condensation of pyridine homologues with quinones and ketones or carboxylic acids can give rise to resinous products very similar in character and appearance to the gum formed in crude shale gasoline and naphtha. The failure of the anthraquinone to react was expected, as it is structurally incapable of reacting to form a product analogous to I. The condensation of pyridine, quinone, and acetyl acetone to give I definitely involves an oxidation step, and in this case it is probable that excess quinone may act as the oxidizing agent. It was for this reason that acetic and formic acids were tested as alternatives for the ketones in the condensation, as they are at a higher stage of oxidation. Their activity in this respect supports the inference that the ketone is oxidized before or during the condensation.

While pyridine and quinoline gave no gum with the quinones in the absence of the ketones or acids, the tar bases recovered from shale gasoline did give small traces of gum. This could be due to α-alkyl groups on the pyridine nucleus supplying the carbon atom otherwise supplied by the carbonyl compound.

However, in the oxidation of shale gasoline and naphtha one must consider the formation of quinones and possibly also ketones in order to explain the very large quantities of gum that can be formed.

Quinones are well known oxidation products of phenols, but do not appear to have been reported as such in gasoline. Moore and Waters have shown [20] that the oxidation of phenols in hydrocarbon solution involves an initial hydrogen transfer reaction which is usually followed by condensation of the phenol residues to give dihydroxy diphenyl derivatives, although, in some cases, dihydroxy diphenyl methanes are formed. Since the phenol residues possess some anionic character, they can be expected to condense readily with the cationic bases present as a first stage in the reaction.

As mentioned previously, both ketones and carboxylic acids have been reported in trace amounts in shale gasolines and naphthas, and their condensation with the tar base–phenol radicle adduct could give a product similar in composition to I. While this does no doubt occur it is probable that other oxygenated products, such as, possibly, olefin peroxides, could also react in a like manner. That such other products can also enter into the reactions is indicated by the gum contents of over 1000 mg/100 ml that can be formed in samples containing only traces of ketones and carboxylic acids. This condensation could also be responsible for the rapid removal of traces of aldehydes and ketones from shale naphthas, and thus explain the negative results that have frequently been reported for these constituents.[21]

In a refined gasoline all traces of the active carbonyl compounds have been removed during the refining process along with the reactive conjugated di-olefins. Consequently the addition of purified (pyrrole-free) tar bases can be expected to give little, if any, gum by oxidative condensation with the phenols present. This is in agreement with the observation that the purified tar bases did not increase gum formation when added to a refined shale gasoline.[2]

Petroleum gasolines and naphthas contain much smaller concentrations of tar bases, phenols, and carbonyl compounds and their precursors than do shale gasolines and naphthas. Consequently, although the proposed gum-forming reaction can take place in the petroleum products, it will naturally do so to a much smaller extent, and other gum-forming reactions can predominate.

At the other extreme coal tar distillates, which contain high concentrations of tar acids and tar bases as well as other oxygen compounds, and reactive olefins, such as *cyclo*pentadiene, indene, and coumarone, rapidly discolour and form large amounts of gum.

That the proposed gum-forming reaction may be active in these products is suggested by the statement that, " Other things being equal, a benzole containing pyridine bases shows a much greater tendency to develop colour than one from which the bases have been removed completely." [22]

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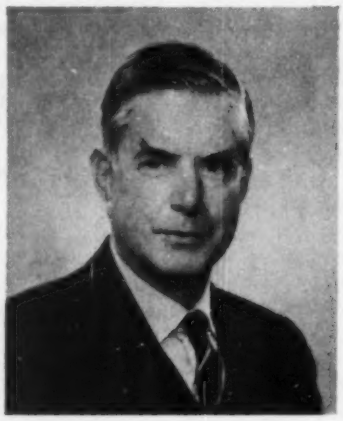
OBITUARY

RALPH JOHN BRESSEY

1905–1960

THE death of R. J. Bressey, Fuel Oil Manager of Shell-Mex and B.P. Ltd, on 27 October 1960, following an operation, came as a great shock to his wide circle of friends and colleagues in the industry.



He entered the oil industry in 1928 as an assistant chemist in the Central Laboratories of Shell-Mex Ltd (as it then was) at Finsbury Circus, where his ability soon became apparent. About a year later he was appointed as chemist and fuel technologist in the Fuel Oil Sales Department, later becoming a Head Office Supervisor, a position he also held in the war-time Petroleum Board. On the resumption of company trading in 1948, he became Assistant Fuel Oil Manager and, in 1952, Fuel Oil Manager.

During the early years of his career Ralph Bressey worked closely with G. R. Llewellyn, in the pioneering days of the high speed compression ignition engine for road vehicles, the development of diesel rail traction and diesel trawlers, and the introduction of butane and propane for industrial purposes, besides contributing to the successful extension of the "black oil" trade into many new and varied applications.

His technical ability was evident from his qualifications as Associate of the Royal Institute of Chemistry, Fellow of the Institute of Fuel, and Fellow of the IP.

Ralph Bressey's place in our memory does not, however, rest solely on his successful business career. We remember him as a man of erudition, with a distinguished record at Oxford, as a modest and sincere friend, a lover of good music, an interesting speaker with charm of manner and an enviable sense of humour, a sympathetic and co-operative chief, and a colleague of considerable business acumen supported by a sound technical background.

The death of this kindly, unassuming and talented colleague, at the age of 55, is indeed untimely, and represents a great loss to the petroleum industry, and to his wife and two children, to whom we extend our deepest sympathy.

C. W. G. M.

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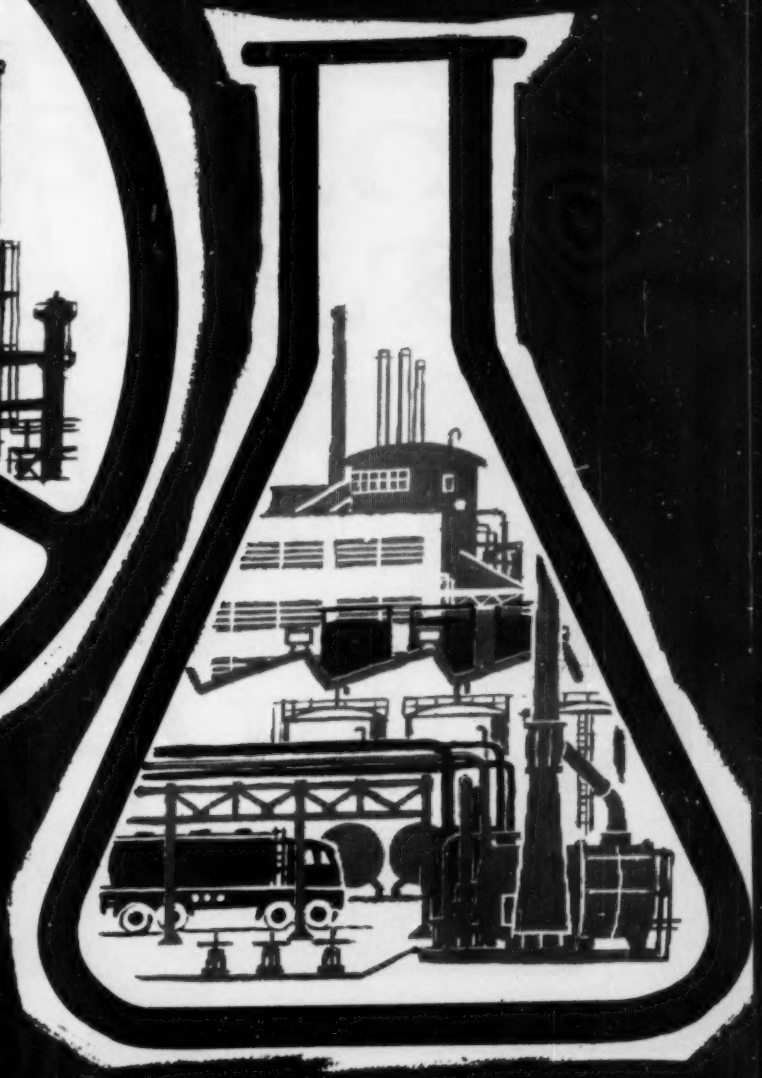

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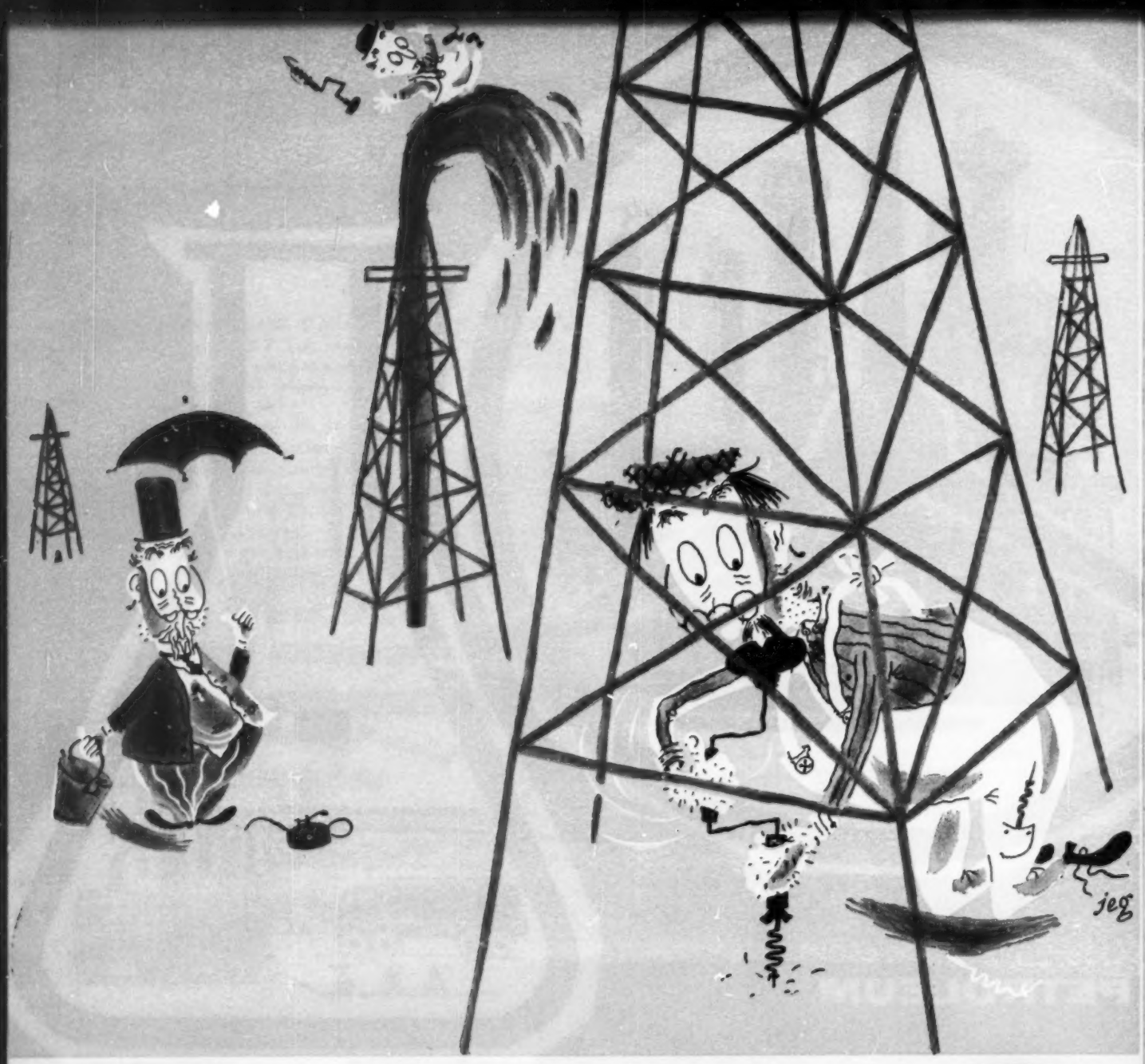

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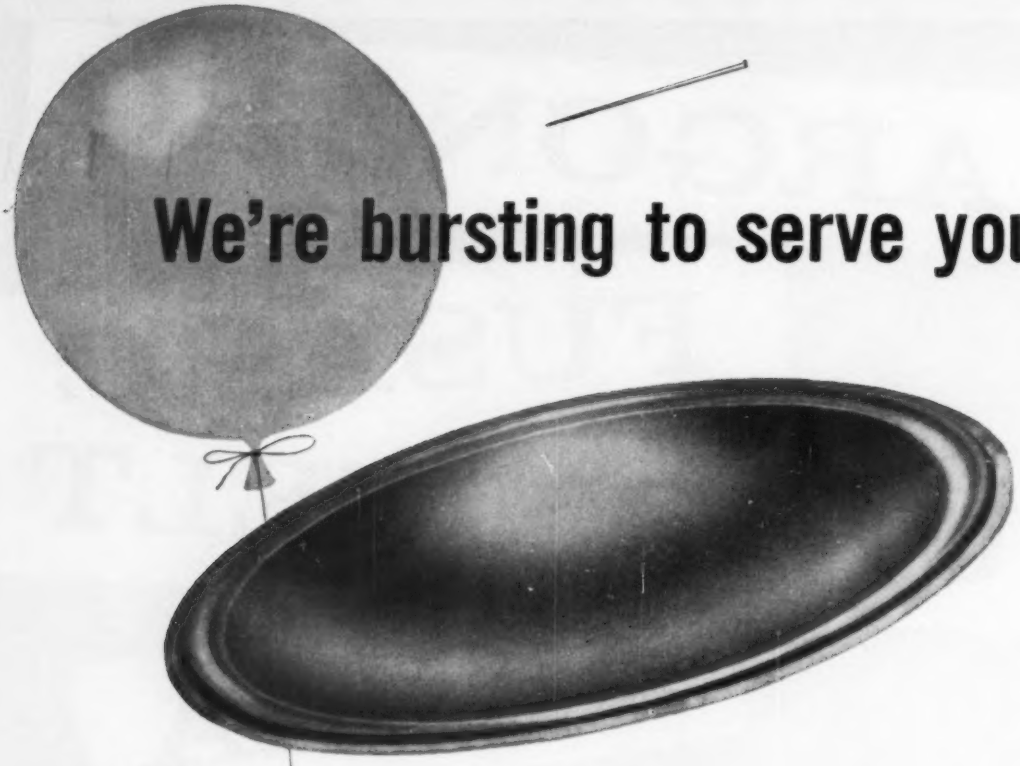

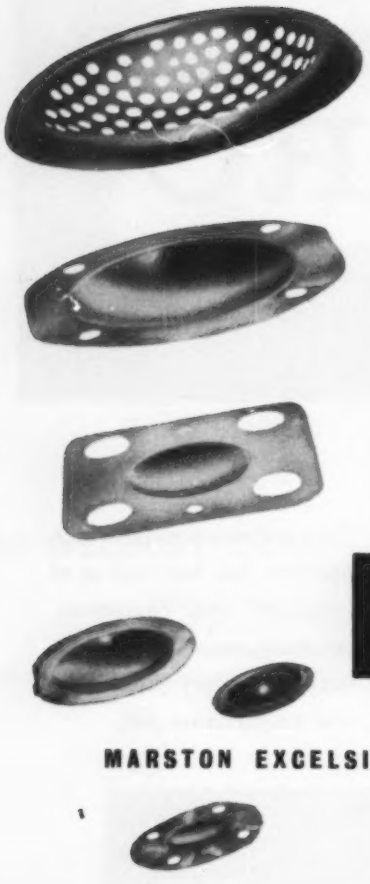

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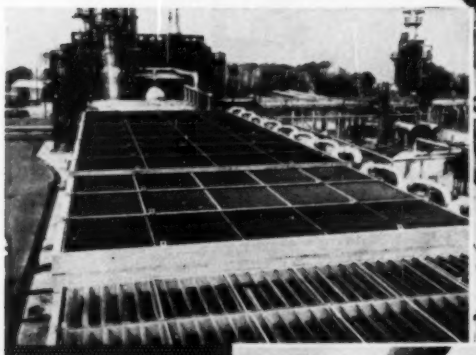

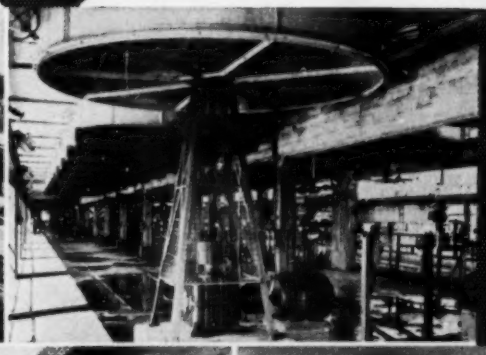

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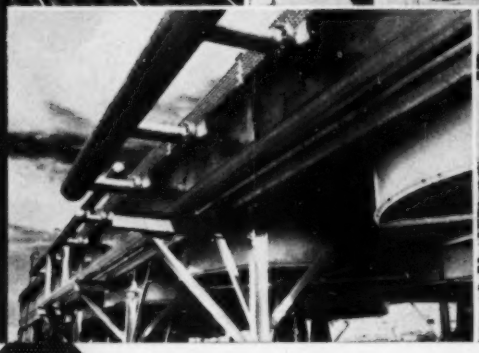

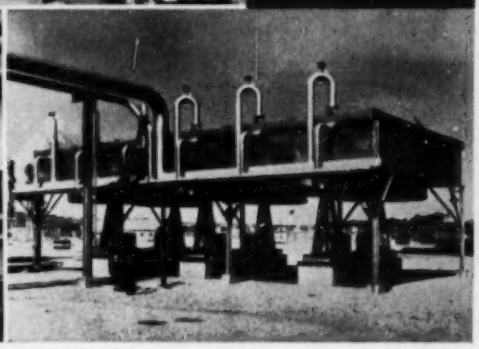

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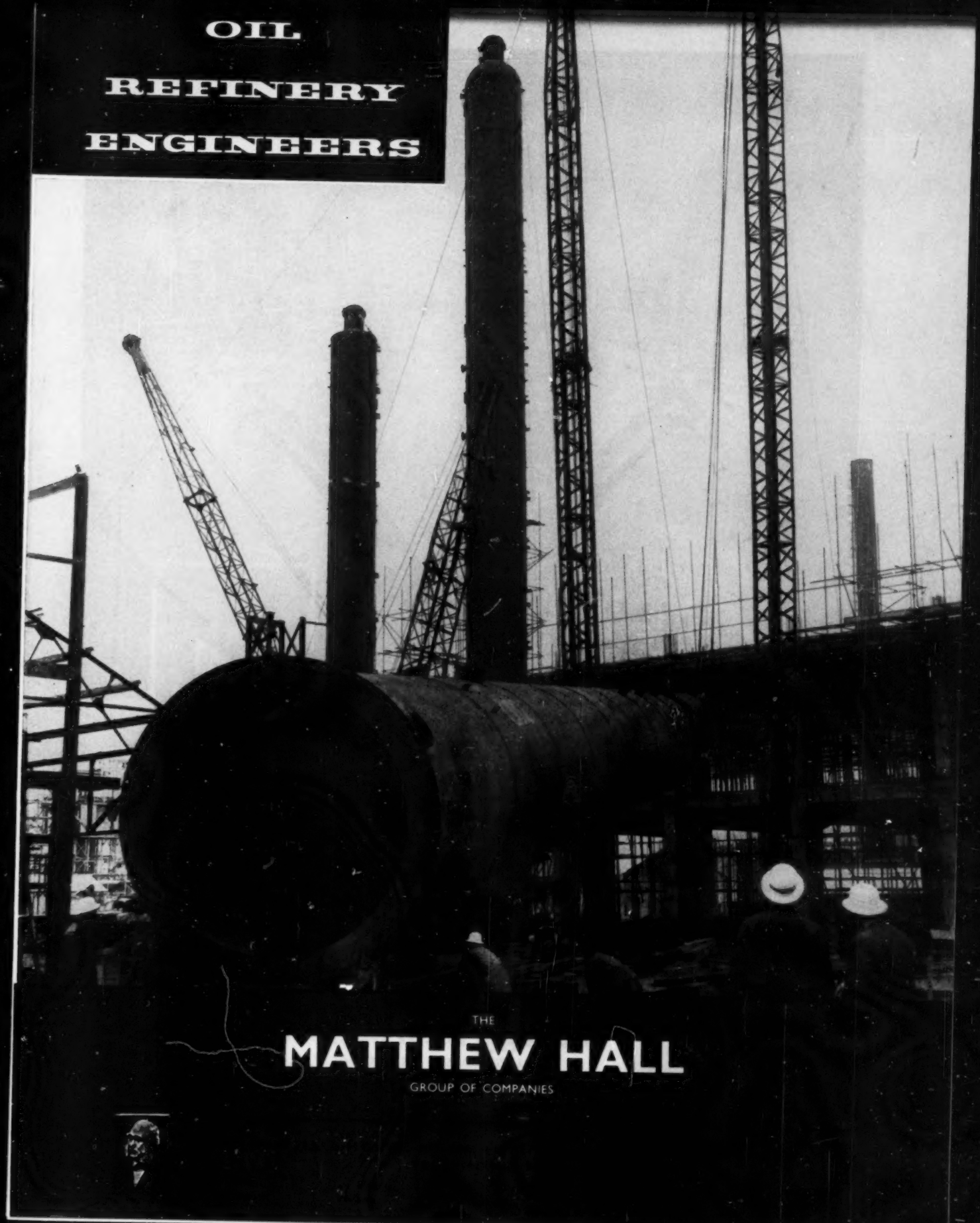

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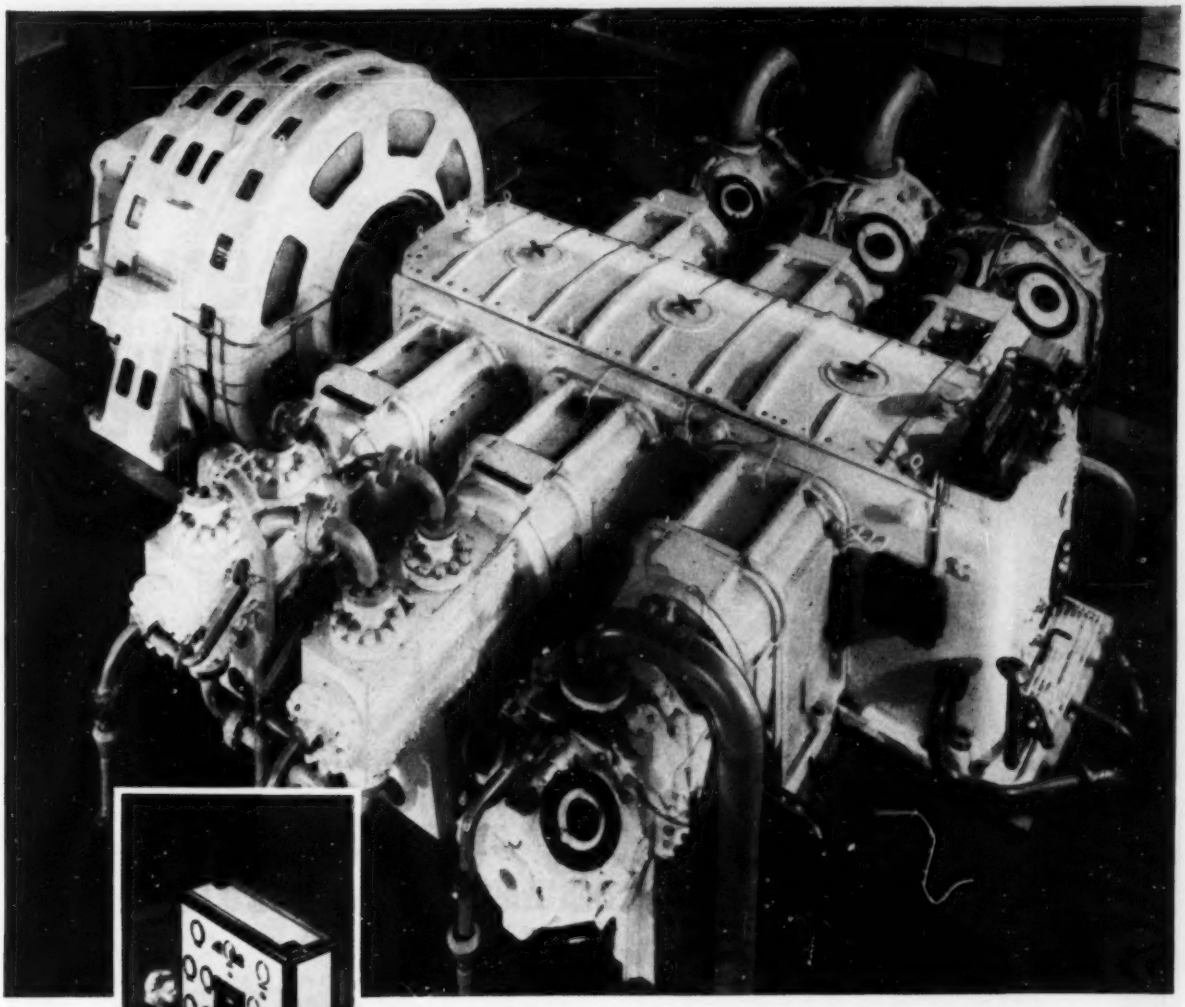

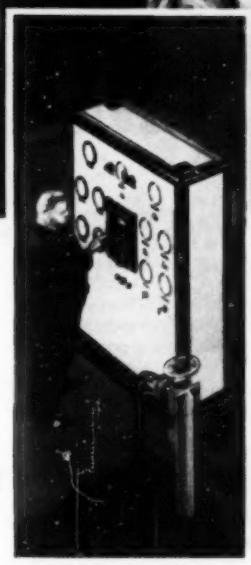

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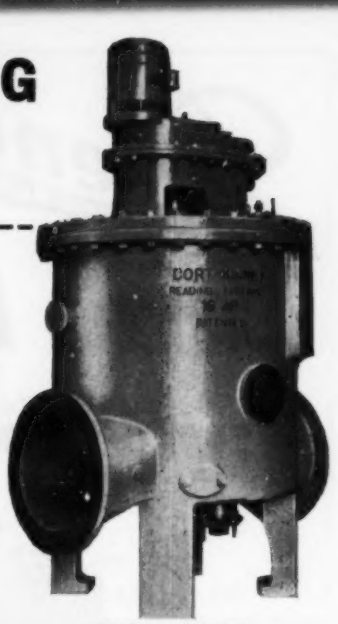

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